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# A Facile Synthesis of Trifluoromethylamines by Oxidative Desulfurization–Fluorination of Dithiocarbamates

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Trifluoromethylamines are easily synthesized from dithiocarbamates by a reagent system consisting of tetrabutylammonium dihydrogentrifluoride and an *N*-halo imide under mild conditions. When this reaction was applied to dithiocarbamates $ArN(R)CS_2Me$ at higher temperatures, the trifluoromethylation was accompanied by halogen substitution at the *p*-position of the Ar group. The synthesis of trifluoromethyl-substituted adenosine is also described.

Because fluorine is the most electronegative element and the van der Waals radius of fluorine is close to that of hydrogen, the introduction of fluorine often improves the properties of the parent compounds and/or induces novel activities.[1] Recently, these effects have been rationally reasoned, and many new fluorinated materials, drugs, and agrochemicals have been designed[2] and synthesized.[3]

In view of the strongly electron-withdrawing nature of a trifluoromethyl group, trifluoromethylamines are apparently much less basic and less nucleophilic than the corresponding methylamines,[4] and thus the physical, chemical, and/or biological properties of trifluoromethylamines should be remarkably modified as compared with those of the corresponding methylamines. For example, aryl(trifluoromethyl)amines resist oxidation compared with the corresponding methylamines, and can be applied to liquid-crystalline materials.[5] Thanks to these properties, trifluoromethylamino-substituted agrochemicals[6] and artificial bloods[7] containing a trifluoromethylamine or perfluoroalkylamine moiety have been developed, and reagents substituted by a trifluoromethylamino group are utilized in organic synthesis as oxidants[8—10] or fluorination reagents.[11]

Preparative methods of trifluoromethylamines are classified into: i) fluorination of *N*-formylamines with $SF_4$ and KF,[12] ii) fluorine substitution of trichloromethylamines with $SbF_3$,[13] iii) fluorination of thiuram sulfides with $SF_4$[14] or $R_2NSF_3$,[15] iv) reaction of secondary amines with $CBr_2F_2$ and tetrakis(dimethylamino)ethylene,[16] v) fluorination of isocyanates with anhydrous hydrogen fluoride,[17] vi) electrochemical fluorination of alkylamines,[18] and vii) electrophilic trifluoromethylation of amines by treatment with *O*-(trifluoromethyl)dibenzofuranium salts.[19] Most of these methods use such highly toxic and/or corrosive reagents as $SF_4$, $SbF_3$, $F_2$, and/or anhydrous hydrogen fluoride under harsh conditions, and the yield of the desired products are not always high enough. These technical problems have hampered the systematic study on trifluoromethylamines.

We have recently demonstrated that *oxidative desulfurization–fluorination reaction* using an *N*-halo imide and a fluoride source is a convenient entry to the synthesis of organofluorine compounds.[20] This reaction allows us to replace a C–S bond with a C–F bond under extremely mild conditions. We have applied this reaction to methyl dithiocarbamates $R^1R^2NC(S)SMe$ to find that trifluoromethylamines $R^1R^2NCF_3$ are readily prepared in good yields.[5a,21] In this paper we report on the experimental details concerning the synthesis of trifluoromethylamines.

## Results and Discussion

**Synthesis of Trifluoromethylamines by the Oxidative Desulfurization–Fluorination of Dithiocarbamates.** Secondary amines **1** were successively treated with butyllithium (*n*-BuLi), $CS_2$ and then with MeI to give corresponding dithiocarbamates **2** in high yields.[22] Oxidative desulfurization–fluorination of dithiocarbamates **2** was carried out using tetrabutylammonium dihydrogentrifluoride ($TBAH_2F_3$) as a fluorinating reagent and an *N*-halo imide (Scheme 1). As summarized in Table 1, trifluoromethylamines **3** were obtained in yields of synthetic meaning.

Initially, we studied the optimization of the conditions using diphenyldithiocarbamate (**2a**) as a model substrate. For a halonium ion agent, we used *N*-bromosuccinimide (NBS), 1,3-dibromo-5,5-dimethylhydantoin (DBH), *N*-chlorosuccinimide (NCS), *N*-iodosuccinimide (NIS), or *N*-bromoacetamide (NBA). Compound **2a** was treated with $TBAH_2F_3$ (5 mol) and one of the *N*-halo imide (4 mol) in dichloromethane at room temperature for 1 h (Table 1, Entries 1 to 5). All of these oxidants were found to promote the reaction to give diphen-

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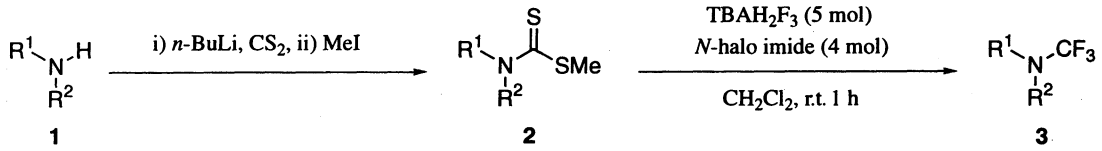
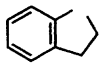



Scheme 1.

Table 1. Synthesis of Trifluoromethylamines **3** or **4** from Dithiocarbamates **2**

| Entry | $R^1$ | $R^2$ | **2** | *N*-Halo imide (mol) | Temp | Yield of **3** or **4** (%)[a] | |
|---|---|---|---|---|---|---|---|
| 1 | Ph | Ph | **2a** | NBS (4) | r.t. | **3a** | 78 |
| 2 | | | | DBH (4) | | | —[b] |
| 3 | | | | NCS (4) | | | 23 |
| 4 | | | | NIS (4) | | | 60 |
| 5 | | | | NBA (4) | | | 36 |
| 6 | 4-MeO-$C_6H_4$ | $PhCH_2$ | **2b** | NBS (4) | | **3b** | 99 |
| 7 | | | | NBS (1.5) | | | 38[c] |
| 8[d] | | | | NBS (4) | | | 84 |
| 9[e] | | | | | | | 70 |
| 10 | 4-Cl-$C_6H_4$ | $PhCH_2$ | **2c** | | | **3c** | 88 |
| 11 | 4-F-$C_6H_4$ | $PhCH_2$ | **2d** | | | **3d** | 84 |
| 12 | 4-NC-$C_6H_4$ | $PhCH_2$ | **2e** | | | **3e** | 78 |
| 13 | | | | DBH (4) | | | 99 |
| 14[f] | | | | NBS (4) | | | 97 |
| 15[g] | | | | | | | 99 |
| 16 | 4-MeO-$C_6H_4$ | Me | **2f** | | | **3f** | 90 |
| 17 | 4-$O_2N$-$C_6H_4$ | Me | **2g** | DBH (4) (NBS) | | **3g** | 96 (68) |
| 18 |  | | **2h** | NBS (4) | | **3h** | 76 |
| 19 | 3-Me-$C_6H_4$ | 3-Me-$C_6H_4$ | **2i** | NIS (4) (NBS[b]) | | **3i** | 74 (48) |
| 20 | 4-Br-2-F-$C_6H_3$ | Me | **2j** | DBH (5) | | **3j** | 87 |
| 21 | | Et | **2k** | | | **3k** | 82 |
| 22 | | *n*-$C_6H_{13}$ | **2l** | | | **3l** | 87 |
| 23 | Ph | Me | **2m** | NBS (4) | | **3m** | 66 |
| 24 | | | | DBH (5) | Reflux | **4m** | 96 |
| 25 | | Et | **2n** | NBS (4) | r.t. | **3n** | 65 |
| 26 | | | | DBH (5) | Refulx | **4n** | 83 |
| 27 | | Pr | **2o** | NBS (4) | r.t. | **3o** | 78 |
| 28 | | | | DBH (5) | Reflux | **4o** | 68 |
| 29 | | *n*-$C_6H_{13}$ | **2p** | NBS (4) | r.t. | **3p** | 68 |
| 30 | | | | DBH (5) | Reflux (0 °C) | **4p** | 71 (86) |
| 31 | | *n*-$C_8H_{17}$ | **2q** | NBS (4) | r.t. | **3q** | 79 |
| 32 | | | | DBH (5) | 0 °C | **4q** | 79 |
| 33[h] | | | | NBS (5) | | | 60 |
| 34[i] | $PhCH_2$ | $PhCH_2$ | **2r** | NBS (4) | r.t. | **3r** | 86 |
| 35[i] | | Pr | **2s** | | | **3s** | 84 |

a) Isolated yields. b) Accompanied by aromatic bromination. c) **2b** was recovered in 54% yield. d) $TBAH_2F_3$ (2 mol) was used. e) $TBAH_2F_3$ (1.2 mol) was used. f) $(HF)_9$/Py (1 mL $mol^{-1}$, 80 mol of $F^-$) was used. g) $(HF)_3/NEt_3$ (0.2 mL $mol^{-1}$, 30 mol of $F^-$) was used. h) $(HF)_9$/Py (0.5 mL $mmol^{-1}$) was used. i) $TBAH_2F_3$ (3 mol) was used.

yl(trifluoromethyl)amine (**3a**). When DBH was used (Entry 2), trifluoromethylation proceeded quantitatively along with bromination of the phenyl ring being accompanied. Among the oxidants, NBS (Entry 1) was concluded to be the most effective for the synthesis of **3a**.

We next examined the amount of $TBAH_2F_3$ (Entries 6, 8, and 9) using **2b** for the substrate. As can be readily seen, when the amount of $TBAH_2F_3$ was reduced to 1.2 mol, **3b** was obtained in a 70% yield (Entry 9). This means that all of the fluorine atoms of $TBAH_2F_3$ can be used for the fluorination. When the same reaction was carried out with $TBAF{\cdot}3H_2O$ (5 mol) and NBS (4 mol), however, a complex mixture of products resulted. Accordingly, $H_2F_3^-$ ion is definitely superior to $F^-$.

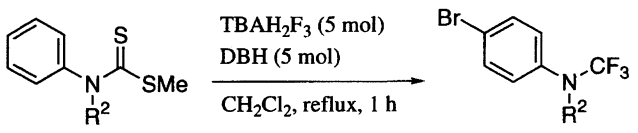
The trifluoromethylamine synthesis was applied to various kinds of cyclic and acyclic dithiocarbamates, and the corresponding trifluoromethylamines **3** could be readily isolated in good-to-excellent yields (Entries 10 to 12, 16 and 18).

When DBH or excess NBS was used as an oxidant, bromination of the aromatic ring also took place (Entries 2 and 19).

For these substrates, NBS (4.0 mol) or NIS was proved to be a reagent of choice (compare Entry 1 with 4; see also Entry 19).

For the substrates bearing an electron-withdrawing group, a combination of $TBAH_2F_3$/DBH or an HF–amine complex/NBS was effective to afford the desired trifluoromethylamine quantitatively (Entries 12 to 15). Upon the use of an HF-amine complex, however, the reaction should be carried out in an effective hood to avoid any contact with hydrogen fluoride; also, it is recommended to use a Teflon® bottle as a reaction vessel. Therefore, a combination of $TBAH_2F_3$/DBH is best for the synthesis of **3** having an electron-withdrawing group (Entries 17 and 20 to 22).

When alkyl(phenyl)dithiocarbamates **2** were treated with $TBAH_2F_3$ (5 mol) and NBS (4 mol) in dichloromethane at room temperature, trifluoromethylation only proceeded to afford compounds **3** in high yields. On the contrary, the reaction using $TBAH_2F_3$ (5 mol) and DBH (5 mol) in refluxing dichloromethane (Eq. 1) gave alkyl(4-bromophenyl)(trifluoromethyl)amines **4** as the sole products (Entries 24, 26, 28, and 30). The formation of trifluorination-bromination products **4** was observed in some cases, even at 0 °C (cf. Entries 30 and 32).




**2** **4** (1)

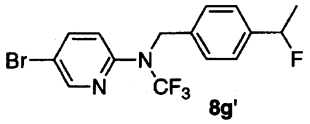
This fluorination reaction is also applicable to the synthesis of dialkyl(trifluoromethyl)amines (Entries 34 and 35) that are readily hydrolyzed upon exposure to moisture. To isolate dialkyl(trifluoromethyl)amines **3r** and **3s**, filtration of insoluble materials generated during the reaction followed by concentration and distillation was suitable.

**Synthesis of Trifluoromethylamino-Substituted Pyridines and Pyrimidines.** The fluorination reaction was applied to the synthesis of 2-(trifluoromethylamino)pyridines and -pyrimidines (Eq. 2). The results, summarized in Table 2, clearly show that trifluoromethylation products **7** (and **11**) or trifluoromethylation–bromination products **8** (and **12**) were obtained in good-to-excellent yields from the corresponding dithiocarbamates **6** (and **10**) by use of $TBAH_2F_3$ (5 mol) and DBH (4—5 mol) in dichloromethane at 0 °C or at the refluxing temperature, respectively.

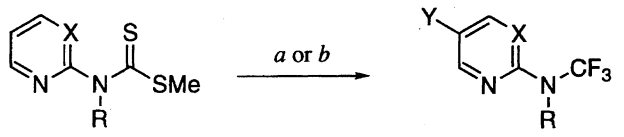
Table 2. Synthesis of Trifluoromethylamino-Substituted Pyridines **7** (or **8**) and Pyrimidines **11** (or **12**)[a]

| Entry | R | X | Carbamate | DBH (mol) | Temp | Product(s) (% yield)[b] | | |
|---|---|---|---|---|---|---|---|---|
| 1 | Me | CH | **6a** | 4 | 0 °C | **7a** | 72 | |
| 2 | | | | 5 | Reflux | **8a** | 78 | |
| 3 | Et | | **6b** | 4 | 0 °C | **7b** | 75 | |
| 4 | | | | 5 | Reflux | **8b** | 82 | |
| 5 | $n$-$C_6H_{13}$ | | **6c** | 4 | 0 °C | **7c** | 67 | |
| 6 | | | | 5 | Reflux | **8c** | 89 | |
| 7 | $n$-$C_8H_{17}$ | | **6d** | 4 | −20 °C | **7d** | 76 | |
| 8 | | | | 5 | Reflux | **8d** | 89 | |
| 9 | $n$-$C_{12}H_{25}$ | | **6e** | 4 | −20 °C | **7e** | 86 | |
| 10 | | | | 5 | Reflux | **8e** | 90 | |
| 11 | $PhCH_2$ | | **6f** | 4 | 0 °C | **7f** | 80 | |
| 12 | | | | 5 | Reflux | **8f** | 78 | |
| 13 | 4-Et-$C_6H_4CH_2$ | | **6g** | 5 | Reflux | **8g** | 41 | **8g′** 38 |
| 14 | Me | N | **10a** | 4 | 0 °C | **11a** | 38 | |
| 15 | | | | 5 | Reflux | **12a** | 84 | |
| 16 | Pr | | **10b** | 4 | 0 °C | **11b** | 50 | |
| 17 | | | | 5 | Reflux | **12b** | 81 | |
| 18 | $n$-$C_6H_{13}$ | | **10c** | 4 | 0 °C | **11c** | 58 | |
| 19 | | | | 5 | Reflux | **12c** | 61 | |
| 20 | $n$-$C_8H_{17}$ | | **10d** | 4 | 0 °C | **11d** | 80 | |
| 21 | | | | 5 | Reflux | **12d** | 24 | **11d** 62 |
| 22 | $n$-$C_{12}H_{25}$ | | **10e** | 4 | 0 °C | **11e** | 63 | |
| 23 | | | | 5 | Reflux | **12e** | 15 | **11e** 65 |

a) All the reactions were carried out with $TBAH_2F_3$ (5 mol), DBH (4—5 mol), in $CH_2Cl_2$ at 0 °C or at its refluxing temperature.
b) Isolated yields.




**8g′**



**6** X = CH
**10** X = N

**7** X = CH, Y = H
**8** X = CH, Y = Br
**11** X = N, Y = H
**12** X = N, Y = Br

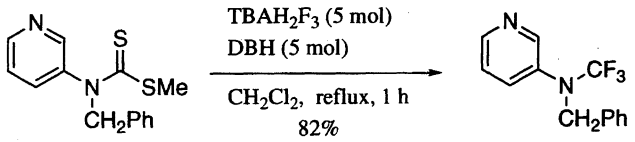
*a*: $TBAH_2F_3$ (5 mol), DBH (4 mol), $CH_2Cl_2$, 0 °C

*b*: $TBAH_2F_3$ (5 mol), DBH (5 mol), $CH_2Cl_2$, reflux

(2)

For the trifluorination of alkyl(2-pyridyl)dithiocarbamates **6**, the reaction conditions using $TBAH_2F_3$ (5 mol) and DBH (4 mol) at 0 °C in dichloromethane was effective, and trifluoromethylamines **7** were obtained in high yields. However, substrates **6d** and **6e** having a long alkyl chain were found to be sensitive to bromination, even at 0 °C. Thus, carrying out the reaction at −20 °C prevented the bromination (Entries 7 and 9), and desired products **7d** and **7e** could be isolated in high yields. When the reaction was performed in refluxing dichloromethane, 2-[alkyl(trifluoromethyl)amino]-5-bromopyridines **8a**—**8g** were obtained in high yields as sole products (Entries 2, 4, 6, 8, 10, 12, and 13); none of the regio isomers or dibrominated compounds were produced. Under similar conditions, alkyl(2-pyrimidinyl)dithiocarbamates **10** were also converted into 2-[alkyl(trifluoromethyl)amino]-pyrimidines **11** or 2-[alkyl(trifluoromethyl)amino]-4-bromopyrimidines **12**, depending on the amount of DBH and the reaction temperature. However, the trifluorination–bromination of **10d** and **10e** having a long alkyl chain (Entries 21 and 23) were sluggish: The aromatic bromination was not completed even at the reflux temperature of dichloromethane. It is noteworthy that some of **6g** was converted into **8g′** under the forcing conditions (Entry 13), probably via benzylic bromination and substitution by fluorine.

An isomer of **7f**, 3-[benzyl(trifluoromethyl)amino]pyridine (**7h**), was prepared in refluxing dichloromethane in high yield from **6h** without bromination (Eq. 3).

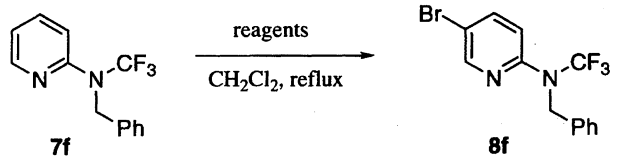


**6h** **7h**

(3)

**Reaction Mechanism.** A plausible reaction mechanism for the oxidative desulfurization–fluorination of dithiocarbamates is shown in Scheme 2. The reaction is assumed to be initiated by an electrophilic attack of a halogen(I) cation towards the sulfur atom of a thiocarbonyl group, followed by a nucleophilic attack of a fluoride ion to the thiocarbonyl carbon to form a C–F bond. The thus formed **14** would undergo a similar electrophilic attack of $X^+$ at sulfur and substitution by a fluoride ion to give **15**. The difluorinated products of type **15** are isolable in the oxidative desulfurization–fluorination of dithiocarbonates.[23] Finally, the remaining MeS group could be substituted in a similar manner to give trifluoromethylated product **3**. The reaction of **2b** with less than 1.5 mol of NBS gave a mixture of trifluoromethylamine **3b** and **2b** in 38 and 54% yields, respectively; none of monofluorinated product **14** or difluorinated product **15** could be detected (Table 1, Entry 7). Based on this observation, the transformations of **2** to **14**, of **14** to **15**, and of **15** to **3** appear to be extremely fast in contrast to the trifluoromethyl ether synthesis.[23]

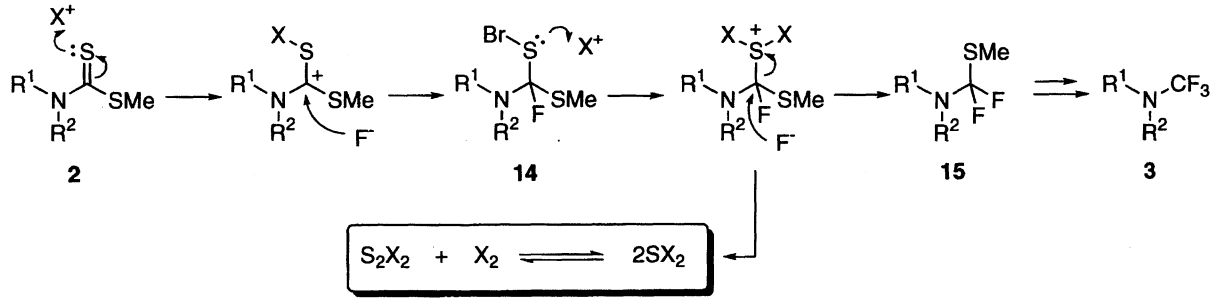
When this reaction was performed at higher temperatures, the trifluorination was accompanied by regioselective ring bromination at the *p*-position (Table 1, Entry 24 to 32 and Table 2). Since the regioselective bromination of the hetero aromatic ring, in particular, attracted our interest; we studied the bromination of **7f** (Eq. 4) in more detail.



**7f** **8f**

(4)

When the bromination of **7f** was performed using DBH (1.2 mol) in refluxing dichloromethane for 6 h, compound **8f** was obtained in only 49% yield. The reaction using $Br_2$ (1.1—2.2 mol) or a reagent system consisting of $TBAH_2F_3$ (2 mol) and DBH (1.2 mol) in refluxing dichloromethane was also ineffective, and the bromination of **7f** was found to



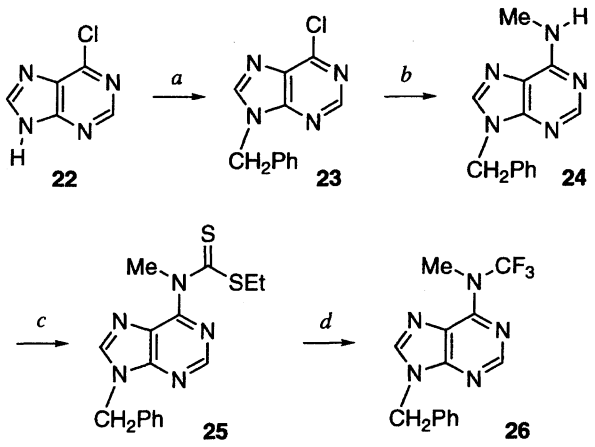

**2** **14** **15** **3**

Scheme 2. A proposed reaction mechanism of trifluoromethylation.

proceed slowly. However, a reaction using a combination of $TBAH_2F_3$ (2 mol) and $Br_2$ (2.2 mol) in refluxing dichloromethane for 1.5 h was quite effective to give **8f** in 84% yield. Therefore, bromination under the oxidative desulfurization-fluorination conditions should be due to $Br_2$, probably in situ generated by a heterolysis of $SBr_2$ (as shown in Scheme 2) and also to $TBAH_2F_3$ acting as a weak base.[24]

**Derivatization of Bromoaryl(trifluoromethyl)amines.** A lithium–bromine exchange of bromoaryl(trifluoromethyl)-amines **4m**, **8a**, and **12a** was readily effected by means of *n*-BuLi at −78 °C, and the resulting aryllithiums were allowed to react with 4-bromobenzaldehyde to give the corresponding adducts **16**, **17**, and **18**, respectively (Scheme 3, route *a*). Methyl esters **19**, **20**, and **21** also were obtained from the bromoaryl(trifluoromethyl)amines by a treatment with *n*-BuLi at −78 °C, followed by carboxylation and esterification (Scheme 3, route *b*). During these transformations, both the trifluoromethylamino group and the aromatic ring remained intact. Thus, transformations of trifluoromethylamines are readily achieved by the use of an additionally introduced bromine functionality.[5]

**Oxidation Potential of Trifluoromethylamines.** The oxidation potential of trifluoromethylamines was measured by cyclic voltammetry. As shown in Table 3, diphenyl(trifluoromethyl)amine (**3a**) showed 1.90 V vs. SCE, 0.94 V higher than methyldiphenylamine (0.96 V), and comparable to diphenyl ether (1.87 V). Similarly, the oxidation potential of 5-bromo-2-[methyl(trifluoromethyl)amino]pyrimidine (**12a**) was 2.32 V vs. SCE, 0.97 V higher than that of corresponding methylamine **25**. Therefore, trifluoromethylamines are highly tolerant of oxidation, as compared with ordinary methylamines, because of delocalization of the lone-pair electrons on nitrogen by a strongly electron-withdrawing trifluoromethyl group.



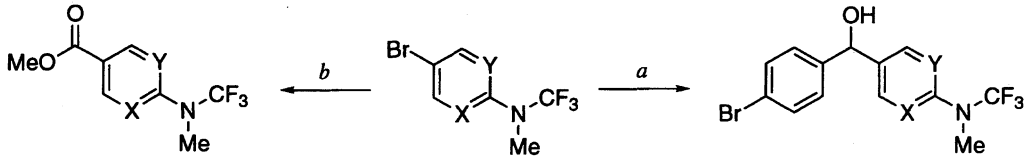

*a*: i) NaH (1.1 mol), DMF, 0 °C to rt, 30 min; ii) BnBr (2.0 mol), 0 °C to rt, 3 h, 69 %.
*b*: $CH_3NH_2$•HCl (5.0 mol), $Et_3N$ (3.0 mol), $CH_2Cl_2$, rt, 12 d, 93%.
*c*: i) *n*-BuLi (1.1 mol), -78 to 0 °C, THF, 1 h; ii) $ClCS_2Et$ (2.0 mol), THF, rt, 2 h, 37%.
*d*: $TBAH_2F_3$ (5.0 mol), DBH (4.0 mol), $CH_2Cl_2$, 0 °C, 1 h, 25%.

Scheme 4. Synthesis of (trifluoromethyl)amino-substituted adenosine **26**.

**Synthesis of Trifluoromethylamino-Substituted Adenosine.** We applied the present reaction to the synthesis of trifluoromethylamino-substituted adenosine derivative **26**. Dithiocarbamate **25** was prepared as shown in Scheme 4, starting with 6-chloropurine (**22**), and was treated with $TBAH_2F_3$ (5 mol) and DBH (4 mol) in dichloromethane at 0 °C for 1 h to give the desired trifluoromethylamine **26** in 25% yield.

## Conclusion

The oxidative desulfurization–fluorination of readily ac-

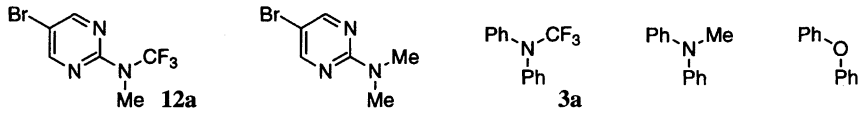



**19** X = Y = CH 98% | **4m** X = Y = CH | **16** X = Y = CH 69%
**20** X = CH, Y = N 43% | **8a** X = CH, Y = N | **17** X = CH, Y = N 78%
**21** X = Y = N 78% | **12a** X = Y = N | **18** X = Y = N 82%

*a*: i) *n*-BuLi (1.1 mol), THF, -78 °C, 0.5 h; ii) *p*-Br-$C_6H_4CHO$ (1.2 mol), -78 °C to rt, 12 h.
*b*: i) *n*-BuLi (1.1 mol), THF, -78 °C, 0.5 h; ii) $CO_2$ (excess), -78 °C to rt; iii) $TMSCHN_2$ (2.0 mol), r.t.

Scheme 3. Reaction of Bromoaryl(trifluoromethyl)amines.

Table 3. Oxidation Potential of (Trifluoromethyl)Amines **3a** and **12a** (vs. SCE)




| 2.32 V | 1.45 V | 1.90 V | 0.96 V | 1.87 V |
|---|---|---|---|---|

cessible dithiocarbamates allows us to synthesize aryl-, heteroaryl-, and alkyl(trifluoromethyl)amines under extremely mild conditions. When the reaction is carried out at higher temperatures, bromination of the heteroaryl group at the *p*-position sometimes takes place regioselectively.

We have also demonstrated that trifluoromethylamines resist oxidation, as compared with the corresponding methylamines. This novel synthetic reaction should find wide applications, particularly in synthetic studies of new drugs, agrochemicals, and opto-electrical materials.

## Experimental

**General.** All of the temperatures are uncorrected. Unless otherwise noted, the reagents and solvents were purchased from Aldrich Chemical Co., Kanto Chemicals, Tokyo Kasei, or Wako Chemicals, Inc. and were used as received. All of the reactions were carried out under an argon atmosphere in a dry, freshly distilled solvent, unless otherwise noted. Tetrahydrofuran (THF) was distilled from sodium/benzophenone, and dimethylformamide (DMF) from calcium hydride. Dichloromethane ($CH_2Cl_2$) was pre-dried with $P_2O_5$ and distilled from calcium hydride. Unless otherwise stated, the yields refer to materials purified by column chromatography or distillation under reduced pressure. The purchased reagents were of the highest commercial quality and used without further purification, unless otherwise noted. Thin layer chromatography was carried out using 0.25 mm E. Merck silica gel plates (Silica Gel $F_{254}$) with a visualizing device of UV light and/or phosphomolybdic acid or *p*-anisaldehyde. Silica gel from E. Merck (Kieselgel 60, 230—400 mesh) or Nacalai Tesque (silica gel 60, 150—325 mesh) were used for flash-column chromatography. Silica gel purchased from E. Merck (Kieselgel 60, 70—230 mesh) or Wako (Wakogel C-200) was used for column chromatography under an atmospheric or slightly positive pressure. Unless otherwise noted, the NMR spectra were measured in a $CDCl_3$ solution. $^1$H NMR, $^{13}$C NMR, and $^{19}$F NMR spectra were recorded on a JEOL FX-100 spectrometer at 100 ($^1$H) and 94 ($^{19}$F) MHz, on a Bruker AC-200 spectrometer at 200 ($^1$H), 50.3 ($^{13}$C), and 188 ($^{19}$F) MHz, or on a Varian Mercury-300 spectrometer at 300 ($^1$H), 75.5 ($^{13}$C), and 282 ($^{19}$F) MHz, respectively. Chemical shifts of $^1$H NMR, $^{13}$C NMR, and $^{19}$F NMR signals are quoted relative to internal standard $Me_4Si$ ($\delta = 0.00$), $CDCl_3$ ($\delta = 77.00$) or $CFCl_3$ ($\delta = 0.00$), respectively, and expressed by chemical shift in ppm ($\delta$), multiplicity, coupling constant (Hz), and relative intensity. The following abbreviations are used to explain the multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, and br = broad. IR spectra were recorded on a Shimadzu FTIR-8100A in neat unless otherwise noted. The mass spectra were recorded on a Shimadzu GC/MS QP-5000 or on a Hitachi H-80 double-focusing tandem gas-chromatography mass spectrometer (70 eV). The melting points were measured with an Olympus BH-2 optical polarizing microscope equipped with a Mettler FP-900 hot-stage. Elemental analyses were carried out by Elemental Analysis Center, Tokyo Institute of Technology, using Yanako MT2 CHN Corder. High-resolution mass spectra were obtained on a JEOL MStation. $TBAH_2F_3$ was prepared according to the literature procedure[25] and dried in vacuo at room temperature overnight right before use.

**General Procedures for the Preparation of Secondary Amines: Method A.**[26] Sodium borohydride (59 mmol) was slowly added portionwise to a stirred suspension of a primary aromatic amine (10 mmol), an aldehyde (11 mmol), acetic acid (8.7 mL), anhydrous sodium acetate (33 mmol), and sodium sulfate (11 mmol) in ethanol (20 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred until all of the amine was consumed. Ethanol and acetic acid were then removed under reduced pressure. The residue was treated with a sodium hydroxide aq. solution (1 M, 30 mL) (1 M = 1 mol dm$^{-3}$) and diethyl ether (100 mL). The organic phase was separated, and the aq. phase was extracted with diethyl ether three times. The combined organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography or bulb-to-bulb distillation to give the desired secondary amine.

**Method B.** A hexane solution of *n*-BuLi (11 mmol) was slowly added to a stirred solution of a primary aromatic amine (10 mmol) in THF (20 mL) at −78 °C. After the solution was allowed to warm to 0 °C over 1 h, an alkyl iodide (20 mmol) was added dropwise to the reaction mixture at 0 °C. The resulting mixture was stirred at room temperature until all of the substrate was consumed and was then treated with aq $NaHCO_3$ solution. The organic phase was separated and the aqueous phase was extracted with diethyl ether three times. The workup and purification described in Method A gave the desired secondary amine.

**Method C.**[27] A suspension of sodium methoxide (50 mmol), paraformaldehyde (14 mmol) and a primary aromatic amine (10 mmol) in methanol (25 mL) was stirred for 15 h at 40 °C before sodium borohydride (10 mmol) was added at room temperature. The resulting mixture was heated at 50 °C for 4 h, and the methanol was removed under reduced pressure. A crude white solid was dissolved in a sat. $NaHCO_3$ aq solution and diethyl ether, and the organic phase was separated. The aqueous phase was extracted with diethyl ether three times. The workup and purification described above gave the desired secondary amine.

**Method D.** To a stirred solution of a substituted 2-chloropyrimidine (35 mmol) in THF (50 mL) was added a 40% solution of an alkylamine in methanol (175 mmol) at 0 °C. The reaction mixture was stirred at 50 °C until all of the substrate was consumed and was poured into a sat. $NaHCO_3$ aq solution. The workup and purification by column chromatography gave the desired 2-(alkylamino)pyrimidine.

Method, isolated yield and spectroscopic properties of products are shown below.

**Benzyl(4-methoxyphenyl)amine (1b).** Method A, 85%. Colorless crystals, mp 40.5—41.5 °C; $R_f = 0.44$ (hexane : $Et_2O$ = 2 : 1). IR (KBr) 3380, 2998, 2950, 2903, 2832, 1642, 1514, 1462, 1441, 1406, 1296, 1238, 1036, 828, 768, 704 cm$^{-1}$; $^1$H NMR (100 MHz) $\delta$ = 3.77 (s, 3 H), 3.78 (br s, 1 H), 4.31 (s, 2 H), 6.63 (d, $J$ = 9 Hz, 2 H), 6.81 (d, $J$ = 9 Hz, 2 H), 7.3—7.4 (m, 5 H); $^{13}$C NMR (75.5 MHz) $\delta$ = 49.2 (s), 55.8 (s), 114.1 (s), 114.8 (s), 127.1 (s), 127.5 (s), 128.5 (s), 139.6 (s), 142.4 (s), 152.1 (s); MS *m/z* (rel intensity) 214 ($M^+$+1; 10), 213 ($M^+$; 59), 212 (11), 211 (25), 196 (28), 122 (88), 107 (6), 106 (7), 105 (7), 95 (14), 91 (100), 77 (13), 65 (27). Found: *m/z* 213.1166. Calcd for $C_{14}H_{15}NO$: M, 213.1154.

**Benzyl(4-chlorophenyl)amine (1c).** Method A, 86%. A pale yellow oil; $R_f = 0.39$ (hexane : EtOAc = 10 : 1). IR 3428, 3063, 2853, 1601, 1505, 1453, 1321, 1296, 1266, 1246, 1179, 1123, 1028, 816, 773, 698 cm$^{-1}$; $^1$H NMR (100 MHz) $\delta$ = 4.07 (br s, 1 H), 4.31 (s, 2 H), 6.55 (d, $J$ = 9 Hz, 2 H), 7.12 (d, $J$ = 9 Hz, 2 H), 7.3—7.4 (m, 5 H); $^{13}$C NMR (50.3 MHz) $\delta$ = 48.3 (s), 113.8 (s), 122.0 (s), 127.3 (s), 127.4 (s), 128.6 (s), 129.0 (s), 138.9 (s), 146.6 (s); MS *m/z* (rel intensity) 219 ($M^+$+2; 10), 218 ($M^+$+1; 6), 217 ($M^+$; 32), 216 ($M^+$−1; 6), 140 (5), 111 (6), 91 (100), 77 (7), 75 (6), 65 (20). Found: *m/z* 217.0662. Calcd for $C_{13}H_{12}ClN$: M, 217.0658.

**Benzyl(4-fluorophenyl)amine (1d).** Method A, 85%. A

colorless oil, bp 185—190 °C/2 mmHg (1 mmHg = 133.322 Pa); $R_f$ = 0.52 (hexane : EtOAc = 5 : 1). IR 3410, 3030, 1618, 1521, 1494, 1450, 1325, 1296, 1275, 1215, 1118, 1075, 1028, 812, 724, 690, 500 $cm^{-1}$; $^1H$ NMR (100 MHz) $\delta$ = 3.94 (br s, 1 H), 4.31 (s, 2 H), 6.58 (dd, $J$ = 4, 9 Hz, 2 H), 6.91 (dd, $J$ = 9, 9 Hz, 2 H), 7.3—7.4 (m, 5 H); $^{19}F$ NMR (94 MHz) $\delta$ = −128.4 (septet, $J$ = 4 Hz); $^{13}C$ NMR (75.5 MHz) $\delta$ = 48.8 (s), 113.6 (d, $J$ = 8 Hz), 115.6 (d, $J$ = 22 Hz), 127.2 (s), 127.4 (s), 128.6 (s), 139.2 (s), 144.4 (d, $J$ = 2 Hz), 155.8 (d, $^1J_{C-F}$ = 235 Hz); MS $m/z$ (rel intensity) 202 ($M^+$+1; 5), 201 ($M^+$; 34), 200 ($M^+$−1; 64), 91 (100). Found: $m/z$ 201.0955. Calcd for $C_{13}H_{12}FN$: M, 201.0954.

**Benzyl(4-cyanophenyl)amine (1e).** Method A, 72%. A pale orange powder, mp 64.4—64.8 °C; $R_f$ = 0.66 (hexane : $Et_2O$ = 1 : 1). IR 3372, 3349, 2215, 1609, 1576, 1534, 1455, 1343, 1296, 1273, 1134, 1028, 830, 814 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta$ = 4.37 (d, $J$ = 6 Hz, 2 H), 4.65 (m, 1 H), 6.59 (d, $J$ = 9 Hz, 2 H), 7.3—7.4 (m, 5 H), 7.42 (d, $J$ = 9 Hz, 2 H); $^{13}C$ NMR (50.3 MHz) $\delta$ = 47.4 (s), 99.0 (s), 112.4 (s), 120.4 (s), 127.3 (s), 127.6 (s), 128.8 (s), 133.7 (s), 137.8 (s), 151.1 (s); MS $m/z$ (rel intensity) 209 ($M^+$+1; 4), 208 ($M^+$; 10), 207 ($M^+$−1; 2), 91 (100). Found: $m/z$ 208.0991. Calcd for $C_{13}H_{12}N_2$: M, 208.1000.

**(4-Bromo-2-fluorophenyl)methylamine (1j).** Method C, 84%. Colorless needles, mp 41.7—42.3 °C; $R_f$ = 0.65 (hexane : $Et_2O$ = 5 : 1). IR (KBr) 3338, 3007, 2878, 2818, 1617, 1584, 1518, 1449, 1410, 1325, 1270, 1196, 1159, 1105, 1046, 873, 860, 803 $cm^{-1}$; $^1H$ NMR (100 MHz) $\delta$ = 2.86 (d, $J$ = 5 Hz, 3 H), 3.93 (br, 1 H), 6.53 (dd, $J$ = 9, 9 Hz, 1 H), 7.04—7.17 (m, 2 H); $^{19}F$ NMR (188 MHz) $\delta$ = −135.0 (dd, $J$ = 7, 9 Hz); $^{13}C$ NMR (50.3 MHz) $\delta$ = 29.9 (s), 106.5 (d, $J$ = 9 Hz), 112.2 (d, $J$ = 4 Hz), 117.1 (d, $J$ = 22 Hz), 127.3 (d, $J$ = 4 Hz), 136.9 (d, $J$ = 12 Hz), 151.1 (d, $^1J_{C-F}$ = 243 Hz); MS $m/z$ (rel intensity) 206 ($M^+$+3; 9), 205 ($M^+$+2; 96), 204 ($M^+$+1; 89), 203 ($M^+$; 100), 202 (96), 163 (13), 161 (13), 157 (14), 155 (15), 123 (17), 122 (11), 103 (20), 94 (18), 82 (10), 81 (14), 77 (14), 76 (14), 75 (19), 74 (12), 63 (13), 62 (13), 61 (16). Found: C, 41.38; H, 3.22; N, 6.85%. Calcd for $C_7H_7BrFN$: C, 41.21; H, 3.46; N, 6.89%.

**(4-Bromo-2-fluorophenyl)ethylamine (1k).** Method B, 84%. A colorless oil, bp 120 °C/0.55 mmHg; $R_f$ = 0.46 (hexane : EtOAc = 10 : 1), 0.18 (hexane : $CH_2Cl_2$ = 4 : 1). IR 3428, 2973, 2874, 1617, 1514, 1483, 1337, 1266, 1194, 1156, 868, 797 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta$ = 1.27 (t, $J$ = 7 Hz, 3 H), 3.15 (qm, $J$ = 7 Hz, 2 H), 3.79 (br s, 1 H), 6.53 (dd, $J$ = 9, 9 Hz, 1 H), 7.06—7.13 (m, 2 H); $^{19}F$ NMR (188 MHz) $\delta$ = −134.7 (t, $J$ = 10 Hz); $^{13}C$ NMR (50.3 MHz) $\delta$ = 14.56 (s), 38.00 (s), 106.6 (d, $J$ = 9 Hz), 112.7 (d, $J$ = 4 Hz), 117.1 (d, $J$ = 22 Hz), 127.4 (d, $J$ = 4 Hz), 136.1 (d, $J$ = 12 Hz), 151.0 (d, $^1J_{C-F}$ = 243 Hz); MS $m/z$ (rel intensity) 220 ($M^+$+3; 5), 219 ($M^+$+2; 58), 218 ($M^+$+1; 9), 217 ($M^+$; 59), 205 (14), 204 (96), 202 (100), 157 (20), 155 (18), 123 (32), 109 (16), 103 (18), 102 (15), 94 (27), 83 (16), 82 (16), 81 (17), 76 (21), 75 (23), 68 (15), 63 (21). Found: C, 44.31; H, 4.34; N, 6.45%. Calcd for $C_8H_9BrFN$: C, 44.06; H, 4.16; N, 6.42%.

**(4-Bromo-2-fluorophenyl)hexylamine (1l).** Method B, 100%. A colorless oil, bp 167 °C/0.5 mmHg; $R_f$ = 0.56 (hexane : EtOAc = 10 : 1). IR 3434, 2930, 2859, 1617, 1514, 1412, 1337, 1267, 1194, 1156, 868, 797 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta$ = 0.97 (t, $J$ = 8 Hz, 3 H), 1.14—1.49 (m, 6 H), 1.49—1.71 (m, 2 H), 3.06 (q, $J$ = 6 Hz, 2 H), 3.82 (br s, 1 H), 6.53 (dd, $J$ = 9, 9 Hz, 1 H), 7.06—7.12 (m, 2 H); $^{19}F$ NMR (188 MHz) $\delta$ = −134.8 (m); $^{13}C$ NMR (50.3 MHz) $\delta$ = 14.0 (s), 22.6 (s), 26.7 (s), 29.3 (s), 31.6 (s), 40.3 (s), 106.4 (d, $J$ = 9 Hz), 112.7 (d, $J$ = 4 Hz), 117.7 (d, $J$ = 22 Hz), 127.4 (d, $J$ = 4 Hz), 136.2 (d, $J$ = 12 Hz), 151.1 (d, $^1J_{C-F}$ = 243 Hz); MS $m/z$ (rel intensity) 276 ($M^+$+3; 8), 275 ($M^+$+2; 57), 274 ($M^+$+1; 8), 273 ($M^+$; 61), 204 (99), 202 (100), 191 (23), 189 (25), 157 (30), 155 (32), 130 (35), 94 (39), 76 (50). Found: $m/z$ 273.0527. Calcd for $C_{12}H_{17}BrFN$: M, 273.0529.

**Benzyl(propyl)amine (1s).** Method B (prepared from benzylamine), 50%. A colorless oil; $R_f$ = 0.36 (hexane : EtOAc : $Et_3N$ = 10 : 10 : 1). IR 3310, 2960, 2932, 2874, 2815, 1605, 1495, 1455, 1379, 1123, 1028, 733, 698 $cm^{-1}$; $^1H$ NMR (300 MHz) $\delta$ = 0.92 (t, $J$ = 8 Hz, 3 H), 1.38 (br s, 1 H), 1.53 (sextet $J$ = 8 Hz, 2 H), 2.60 (t, $J$ = 8 Hz, 2 H), 3.79 (s, 2 H), 7.20—7.38 (m, 5 H); $^{13}C$ NMR (50.3 MHz) $\delta$ = 11.8 (s), 23.2 (s), 51.3 (s), 54.0 (s), 126.8 (s), 128.0 (s), 128.3 (s), 140.5 (s); MS $m/z$ (rel intensity) 149 ($M^+$; 7), 120 (43), 92 (7), 91 (100), 65 (14). Found: $m/z$ 149.1207. Calcd for $C_{10}H_{15}N$: M, 149.1204.

**Ethyl(2-pyridyl)amine (5b).** Method B, 55%. A colorless oil, bp 105 °C/7 mmHg; $R_f$ = 0.67 (hexane : EtOAc = 1 : 3). IR 3420, 3264, 2971, 2361, 1603, 1512, 1447, 1329, 1287, 1154, 1090, 984, 772, 735 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta$ = 1.25 (t, $J$ = 7 Hz, 3 H), 3.29 (dq, $J$ = 6, 7 Hz, 2 H), 4.50 (br s, 1 H), 6.36 (ddm, $J$ = 1, 8 Hz, 1 H), 6.54 (ddd, $J$ = 1, 5, 7 Hz, 1 H), 7.40 (ddm, $J$ = 2, 7 Hz, 1 H), 8.07 (dm, $J$ = 5 Hz, 1 H); $^{13}C$ NMR (50.3 MHz) $\delta$ = 12.9 (s), 42.3 (s), 105.4 (s), 110.7 (s), 136.9 (s), 148.1 (s), 157.5 (s); MS $m/z$ (rel intensity) 123 ($M^+$+1; 9), 122 ($M^+$; 54), 121 (31), 107 (63), 94 (47), 80 (41), 79 (100), 67 (42), 66 (29). Found: C, 68.49; H, 8.13; N, 22.95%. Calcd for $C_7H_{10}N_2$: C, 68.82; H, 8.25; N, 22.93%. Found: $m/z$ 122.0844. Calcd for $C_7H_{10}N_2$: M, 122.0844.

**Hexyl(2-pyridyl)amine (5c).** Method B, 63%. A pale red oil; $R_f$ = 0.75 ($Et_2O$ : EtOAc = 1 : 1). IR 3292, 2957, 2929, 2859, 1703, 1682, 1611, 1518, 1445, 1366, 1282, 1155, 770, 734 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta$ = 0.88 (t, $J$ = 7 Hz, 3 H), 1.30—1.65 (m, 8 H), 3.18 (t, $J$ = 7 Hz, 2 H), 4.40 (br s, 1 H), 6.42—6.60 (m, 2 H), 7.51 (ddd, $J$ = 2, 7, 9 Hz, 1 H), 7.88 (dm, $J$ = 5 Hz, 1 H); $^{13}C$ NMR (50.3 MHz) $\delta$ = 13.9 (s), 22.5 (s), 26.6 (s), 29.0 (s), 31.4 (s), 42.3 (s), 106.5 (s), 111.6 (s), 139.1 (s), 144.7 (s), 157.9 (s); MS $m/z$ (rel intensity) 179 ($M^+$+1; 7), 178 ($M^+$; 48), 163 (4), 141 (12), 135 (10), 121 (64), 107 (100), 94 (85), 78 (61). Found: $m/z$ 178.1472. Calcd for $C_{11}H_{18}N_2$: M, 178.1470.

**Octyl(2-pyridyl)amine (5d).** Method B, 51%. Colorless needles, mp 40.8—41.1 °C; $R_f$ = 0.30 (hexane : $Et_2O$ = 1 : 1). IR (KBr) 3257, 2955, 2924, 2854, 1605, 1574, 1531, 1441, 1292, 1156, 768 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta$ = 0.88 (t, $J$ = 7 Hz, 3 H), 1.27—1.64 (m, 12 H), 3.23 (td, $J$ = 6, 7 Hz, 2 H), 4.44 (br, 1 H), 6.35 (d, $J$ = 8 Hz, 1 H), 6.54 (ddd, $J$ = 2, 5, 7 Hz, 1 H), 7.40 (ddd, $J$ = 2, 7, 8 Hz, 1 H), 8.06 (dm, $J$ = 5 Hz, 1 H); $^{13}C$ NMR (50.3 MHz) $\delta$ = 14.0 (s), 22.6 (s), 27.1 (s), 29.2 (s), 29.3 (s), 29.5 (s), 31.8 (s), 42.3 (s), 106.2 (s), 112.5 (s), 137.3 (s), 148.2 (s), 159.0 (s); MS $m/z$ (rel intensity) 207 ($M^+$+1; 4), 206 ($M^+$; 26), 190 (7), 177 (6), 163 (8), 149 (10), 121 (44), 107 (100), 94 (74), 78 (40). Found: $m/z$ 206.1768. Calcd for $C_{13}H_{22}N_2$: M, 206.1783.

**Dodecyl(2-pyridyl)amine (5e).** Method B, 45%. Colorless needles, mp 58.9—59.7 °C; $R_f$ = 0.40 (hexane : $Et_2O$ = 1 : 1). IR (KBr) 3257, 2955, 2919, 2877, 1606, 1574, 1531, 1470, 1454, 1441, 1332, 1293, 1156, 1136, 1079, 984, 767, 735, 720 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta$ = 0.88 (t, $J$ = 7 Hz, 3 H), 1.26—1.65 (m, 20 H), 3.23 (td, $J$ = 6, 7 Hz, 2 H), 4.42 (br s, 1 H), 6.35 (ddd, $J$ = 1, 2, 9 Hz, 1 H), 6.53 (ddd, $J$ = 1, 5, 7 Hz, 1 H), 7.39 (ddd, $J$ = 2, 7, 9 Hz, 1 H), 8.44 (ddd, $J$ = 1, 2, 5 Hz, 1 H); $^{13}C$ NMR (50.3 MHz) $\delta$ = 14.1 (s), 22.6 (s), 27.1 (s), 29.4 (s), 31.9 (s), 42.3 (s), 106.2 (s), 112.5 (s), 137.3 (s), 148.2 (s), 159.0 (s); MS $m/z$ (rel intensity) 262 ($M^+$; 11), 246 (5), 177 (4), 163 (4), 146 (7), 135 (4), 122 (4), 121 (27), 108 (34), 107 (100), 94 (56), 78 (18). Found: $m/z$ 262.2408. Calcd for $C_{17}H_{30}N_2$: M, 262.2409.

**Ethylbenzyl(2-pyridyl)amine (5g).** Method B, 23%. Color-

less needles, mp 80.8—81.2 °C; $R_f$ = 0.56 (hexane : $Et_2O$ = 1 : 3). IR (KBr) 3241, 3094, 2965, 2928, 2870, 1929, 1601, 1574, 1532, 1455, 1442, 1422, 1335, 1293, 1156, 1125, 1080, 982, 818, 768 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta$ = 1.23 (t, $J$ = 8 Hz, 3 H), 2.64 (t, $J$ = 8 Hz, 2 H), 4.46 (d, $J$ = 6 Hz, 2 H), 4.80 (br s, 1 H), 6.37 (ddd, $J$ = 1, 1, 8 Hz, 1 H), 6.58 (ddd, $J$ = 1, 5, 7 Hz, 1 H), 7.17 (d, $J$ = 9 Hz, 2 H), 7.28 (d, $J$ = 9 Hz, 1 H), 7.40 (ddd, $J$ = 2, 7, 8 Hz, 1 H), 8.11 (ddd, $J$ = 1, 2, 5 Hz, 1 H); $^{13}C$ NMR (50.3 MHz) $\delta$ = 15.6 (s), 28.5 (s), 46.1 (s), 106.7 (s), 120.0 (s), 127.4 (s), 128.1 (s), 136.3 (s), 137.3 (s), 143.2 (s), 148.2 (s), 158.7 (s); MS *m/z* (rel intensity) 213 ($M^+$+1; 8), 212 ($M^+$; 49), 211 (23), 183 (23), 134 (100), 119 (45), 117 (14), 105 (15), 104 (13), 91 (52), 79 (61), 78 (65), 77 (25), 62 (11). Found: *m/z* 212.1320. Calcd for $C_{14}H_{16}N_2$: M, 212.1313.

**Benzyl(3-pyridyl)amine (5h).** Method A, 78%. Colorless needles, mp 88.3—89.4 °C; $R_f$ = 0.59 ($Et_2O$ : methanol = 10 : 1). IR (KBr) 3263, 3098, 3029, 1591, 1578, 1528, 1485, 1450, 1327, 1317, 1303, 1244, 1120, 1069, 1029, 1008, 903, 798, 713, 702 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta$ = 4.05—4.32 (br s, 1 H), 4.33 (d, $J$ = 5 Hz, 2 H), 6.85 (ddd, $J$ = 1, 3, 8 Hz, 1 H), 7.05 (ddd, $J$ = 1, 5, 8 Hz, 1 H), 7.27—7.36 (m, 5 H), 7.95 (dd, $J$ = 1, 5 Hz, 1 H), 8.06 (dd, $J$ = 1, 3 Hz, 1 H); $^{13}C$ NMR (50.3 MHz) $\delta$ = 47.7 (s), 118.5 (s), 123.8 (s), 127.4 (s), 127.4 (s), 128.8 (s), 136.2 (s), 138.6 (s), 138.8 (s), 144.3 (s); MS *m/z* (rel intensity) 185 ($M^+$+1; 4), 184 ($M^+$; 33), 107 (5), 91 (100), 78 (18). Found: *m/z* 184.1002. Calcd for $C_{12}H_{12}N_2$: M, 184.1000.

**2-(Methylamino)pyrimidine (9a).** Method D, 91%. Colorless needles, mp 63.1—63.9 °C; $R_f$ = 0.16 (hexane : $Et_2O$ = 5 : 1). IR (KBr) 2964, 2934, 2876, 1606, 1534, 1510, 1409, 1328, 1284, 1253, 1242, 1178, 1069, 971, 838, 827 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta$ = 3.00 (d, $J$ = 5 Hz, 3 H), 4.65—5.30 (br, 1 H), 6.52 (t, $J$ = 5 Hz, 1 H), 8.29 (d, $J$ = 5 Hz, 2 H); $^{13}C$ NMR (50.3 MHz) $\delta$ = 28.0 (s), 109.7 (s), 157.7 (s), 162.9 (s); MS *m/z* (rel intensity) 110 ($M^+$+1; 13), 109 ($M^+$; 100), 108 (66), 81 (73), 80 (76). Found: *m/z* 109.0641. Calcd for $C_5H_7N_3$: M, 109.0640.

**2-(Propylamino)pyrimidine (9b).** Method D, 82%. A colorless oil; $R_f$ = 0.64 ($Et_2O$). IR 3278, 3110, 2963, 2934, 2874, 1593, 1566, 1538, 1456, 1418, 1367, 1294, 1242, 1150, 1075, 803, 779 $cm^{-1}$; $^1H$ NMR (300 MHz) $\delta$ = 0.98 (t, $J$ = 7 Hz, 3 H), 1.64 (sextet, $J$ = 7 Hz, 2 H), 3.37 (q, $J$ = 7 Hz, 2 H), 5.98 (br s, 1 H), 6.48 (t, $J$ = 5 Hz, 1 H) 8.26 (d, $J$ = 5 Hz, 2 H); $^{13}C$ NMR (75.5 MHz) $\delta$ = 11.3 (s), 22.6 (s), 43.1 (s), 109.9 (s), 157.8 (s), 162.4 (s); MS *m/z* (rel intensity) 138 ($M^+$+1; 4), 137 ($M^+$; 29), 136 ($M^+$−1; 3), 122 (9), 109 (13), 107 (100), 95 (26), 81 (23), 80 (7), 79 (20), 71 (14), 70 (12), 69 (18), 67 (11). Found: *m/z* 137.0954. Calcd for $C_7H_{11}N_3$: M, 137.0953.

**2-(Hexylamino)pyrimidine (9c).** Method D, 95%. A pale yellow oil; $R_f$ = 0.45 ($Et_2O$ : $CH_2Cl_2$ = 1 : 5). IR 3275, 2956, 2930, 2869, 2858, 1590, 1538, 1456, 1416, 1369, 1261, 802, 779, 732, 641 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta$ = 0.88 (t, $J$ = 6 Hz, 3 H), 1.13—1.78 (m, 8 H), 3.29—3.51 (m, 2 H), 5.17—5.23 (br, 1 H), 6.50 (t, $J$ = 5 Hz, 1 H), 8.26 (d, $J$ = 5 Hz, 2 H); $^{13}C$ NMR (50.3 MHz) $\delta$ = 14.0 (s), 22.5 (s), 26.6 (s), 29.5 (s), 31.5 (s), 41.5 (s), 110.1 (s), 157.9 (s), 162.4 (s); MS *m/z* (rel intensity) 179 ($M^+$; 20), 136 (4), 122 (12), 109 (22), 108 (100), 96 (4), 95 (18), 79 (20). Found: *m/z* 179.1417. Calcd for $C_{10}H_{17}N_3$: M, 179.1422.

**2-(Octylamino)pyrimidine (9d).** Method D, 88%. A pale yellow oil; $R_f$ = 0.56 ($Et_2O$ : $CH_2Cl_2$ = 1 : 2). IR 3283, 2956, 2856, 2827, 1596, 1538, 1457, 1416, 1370, 802 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta$ = 0.75—1.05 (m, 3 H), 1.20—1.72 (m, 12 H), 3.29—3.48 (m, 2 H), 4.95—5.25 (br, 1 H), 6.54 (t, $J$ = 5 Hz, 1 H), 8.26 (d, $J$ = 5 Hz, 2 H); $^{13}C$ NMR (50.3 MHz) $\delta$ = 22.5 (s), 26.9 (s), 29.2 (s), 29.3 (s), 29.5 (s), 31.7 (s), 41.4 (s), 110.0 (s), 157.8 (s), 162.5 (s); MS *m/z* (rel intensity) 208 ($M^+$+1; 4), 207 ($M^+$; 29), 122 (20), 109 (39), 108 (100), 96 (9), 95 (27), 79 (12). Found: *m/z* 207.1745. Calcd for $C_{12}H_{21}N_3$: M, 207.1735.

**2-(Dodecylamino)pyrimidine (9e).** Method D, 84%. Colorless needles, mp 51.3—51.9 °C; $R_f$ = 0.34 (hexane : EtOAc = 3 : 1). IR (KBr) 3258, 3022, 2966, 2915, 2851, 1599, 1580, 1538, 1533, 1471, 1459, 1419, 1370, 800, 780, 716, 643 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta$ = 0.87 (t, $J$ = 5 Hz, 3 H), 1.02—1.78 (m, 20 H), 3.38 (q, $J$ = 6 Hz, 2 H), 5.05—5.14 (br, 1 H), 6.48 (t, $J$ = 5 Hz, 1 H), 8.25 (d, $J$ = 5 Hz, 2 H); $^{13}C$ NMR (50.3 MHz) $\delta$ = 14.0 (s), 22.6 (s), 26.9 (s), 29.3 (s), 29.6 (s), 31.8 (s), 41.4 (s), 110.0 (s), 157.9 (s), 162.5 (s); MS *m/z* (rel intensity) 263 ($M^+$; 13), 150 (6), 136 (5), 122 (12), 108 (100), 96 (9), 95 (17). Found: *m/z* 263.2362. Calcd for $C_{16}H_{29}N_3$: M, 263.2361.

**A General Procedure for the Preparation of Dithiocarbamates:** Butyllithium (12 mmol) was slowly added dropwise to a stirred solution of secondary amine **1**, **5**, **9**, or **13** (10 mmol) in THF (20 mL) at −10 °C. After the solution was allowed to warm to 0 °C in 1 h, carbon disulfide (20 mmol) was added dropwise to this mixture at 0 °C. The mixture was stirred for 12 h at room temperature, and methyl iodide (20 mmol) was added dropwise to the reaction mixture at 0 °C. The mixture was stirred at room temperature for 3—5 h and was then treated with sat. $NaHCO_3$ aq solution. The organic phase was separated, and the aq phase was extracted with diethyl ether three times. The combined organic phase was dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography or recrystallization to give the desired dithiocarbamates. The yields and spectra of the products are as follows.

**Methyl *N*,*N*-Diphenyldithiocarbamate (2a).** Yield: 83%. A pale yellow powder, mp 128.3—128.7 °C; $R_f$ = 0.40 (hexane : EtOAc = 10 : 1). IR (KBr) 3080, 3050, 3028, 3000, 2908, 1582, 1484, 1448, 1418, 1354, 1312, 1264, 1161, 1148, 1070, 1048, 1020, 1000, 956, 910, 889, 759, 743, 700, 690 $cm^{-1}$; $^1H$ NMR (90 MHz) $\delta$ = 2.56 (s, 3 H), 7.39 (m, 10 H); $^{13}C$ NMR (75.5 MHz) $\delta$ = 20.9 (s), 127.9 (s), 128.3 (s), 129.6 (s), 145.2 (m), 202.0 (s); MS *m/z* (rel intensity) 260 ($M^+$+1; 2), 259 ($M^+$; 10), 212 (19), 167 (13), 151 (11), 150 (100), 135 (8), 109 (30), 91 (45), 77 (45), 65 (9). Found: *m/z* 259.0492. Calcd for $C_{14}H_{13}NS_2$: M, 259.0489.

**Methyl *N*-Benzyl-*N*-(4-methoxyphenyl)dithiocarbamate (2b).** Yield: 97%. A brown oil; $R_f$ = 0.46 (hexane : $Et_2O$ = 2 : 1). IR 3052, 3028, 3000, 2951, 2910, 2832, 1720, 1602, 1580, 1503, 1429, 1391, 1350, 1296, 1248, 1205, 1180, 1168, 1100, 1078, 1028, 980, 958, 908, 832, 758, 724, 699, 648, 621 $cm^{-1}$; $^1H$ NMR (90 MHz) $\delta$ = 2.57 (s, 3 H), 3.80 (s, 3 H), 5.58 (s, 2 H), 6.84 (d, $J$ = 9 Hz, 2 H), 6.93 (d, $J$ = 9 Hz, 2 H), 7.2—7.3 (m, 5 H); MS *m/z* (rel intensity) 303 ($M^+$; 4), 165 (4), 164 (7), 92 (11), 91 (100), 65 (12). Found: *m/z* 303.0754. Calcd for $C_{16}H_{17}ONS_2$: M, 303.0752.

**Methyl *N*-Benzyl-*N*-(4-chlorophenyl)dithiocarbamate (2c).** Yield: 86%. A pale brown oil; $R_f$ = 0.54 (hexane : $Et_2O$ = 3 : 1). IR 2917, 1603, 1487, 1455, 1387, 1350, 1242, 1206, 1102, 1088, 1015, 957, 833, 700 $cm^{-1}$; $^1H$ NMR (300 MHz) $\delta$ = 2.56 (s, 3 H), 5.56 (s, 2 H), 6.95 (d, $J$ = 9 Hz, 2 H), 7.27 (s, 5 H), 7.32 (d, $J$ = 9 Hz, 2 H); $^{13}C$ NMR (75.5 MHz) $\delta$ = 20.9 (s), 60.4 (s), 127.8 (s), 128.4 (s), 128.7 (s), 129.5 (s), 129.6 (s), 135.0 (s), 135.5 (s), 141.1 (m), 201.9 (s); MS *m/z* (rel intensity) 310 ($M^+$+3; 0.4), 309 ($M^+$+2; 2), 308 ($M^+$+1; 1), 307 ($M^+$; 6), 164 (12), 91 (100). Found: *m/z* 307.0265. Calcd for $C_{15}H_{14}ClNS_2$: M, 307.0256.

**Methyl *N*-Benzyl-*N*-(4-fluorophenyl)dithiocarbamate (2d).** Yield: 90%. A brown oil; $R_f$ = 0.33 (hexane : EtOAc = 10 : 1). IR 3054, 3024, 2910, 1600, 1500, 1432, 1388, 1348, 1238, 1203, 1152, 1100, 1078, 953, 838, 764, 720, 699 $cm^{-1}$; $^1H$ NMR (90

MHz) $\delta$ = 2.58 (s, 3 H), 5.58 (s, 2 H), 7.0—7.1 (m, 4 H), 7.28 (s, 5 H); $^{19}$F NMR (188 MHz) $\delta$ = −111.62 (m); $^{13}$C NMR (75.5 MHz) $\delta$ = 21.0 (s), 60.6 (s), 116.4 (d, $J$ = 23 Hz), 127.9 (s), 128.5 (s), 128.8 (s), 130.1 (d, $J$ = 9 Hz), 135.6 (s), 138.6 (m), 162.4 (d, $^1J_{C-F}$ = 245 Hz), 202.2 (s); MS *m/z* (rel intensity) 293 ($M^+$+2; 1), 292 ($M^+$+1; 1), 291 ($M^+$; 6), 91 (100). Found: *m/z* 291.0571. Calcd for $C_{15}H_{14}FNS_2$: M, 291.0552.

**Methyl *N*-Benzyl-*N*-(4-cyanophenyl)dithiocarbamate (2e).** Yield: 88%. Brown needles, mp 65.7—67.2 °C; $R_f$ = 0.24 (hexane : EtOAc = 10 : 1). IR (KBr) 3080, 3052, 3025, 2950, 2352, 2225, 1596, 1496, 1452, 1380, 1346, 1222, 1204, 1092, 964, 952, 852, 838, 758, 737, 700 cm$^{-1}$; $^1$H NMR (90 MHz) $\delta$ = 2.58 (s, 3 H), 5.58 (s, 2 H), 7.0—7.1 (m, 4 H), 7.28 (s, 5 H); $^{13}$C NMR (75.5 MHz) $\delta$ = 20.9 (s), 60.1 (s), 112.8 (s), 117.7 (s), 128.0 (s), 128.5 (s), 129.3 (s), 133.3 (s), 135.0 (s), 146.6 (m), 201.4 (s); MS *m/z* (rel intensity) 300 ($M^+$+2; 1), 299 ($M^+$+1; 2), 298 ($M^+$; 9), 91 (100). Found: *m/z* 298.0603. Calcd for $C_{16}H_{14}N_2S_2$: M, 298.0598.

**Methyl *N*-(4-Methoxyphenyl)-*N*-methyldithiocarbamate (2f).** Yield: 68%. Colorless needles, mp 93.7—94.6 °C; $R_f$ = 0.42 (hexane : benzene = 1 : 1). IR (KBr) 3050, 3000, 2950, 2920, 2832, 1600, 1504, 1479, 1440, 1420, 1362, 1298, 1243, 1186, 1169, 1096, 1030, 948, 840, 752, 720 cm$^{-1}$; $^1$H NMR (90 MHz) $\delta$ = 2.53 (s, 3 H), 3.76 (s, 3 H), 3.85 (s, 3 H), 7.00 (d, $J$ = 8 Hz, 2 H), 7.18 (d, $J$ = 8 Hz, 2 H); $^{13}$C NMR (75.5 MHz) $\delta$ = 20.8 (s), 46.2 (s), 55.4 (s), 114.7 (s), 127.9 (s), 137.4 (m), 159.6 (s), 200.8 (s); MS *m/z* (rel intensity) 228 ($M^+$+1; 3), 227 ($M^+$; 12), 186 (9), 180 (10), 165 (28), 139 (9), 136 (10), 122 (7), 91 (17), 88 (100), 77 (9), 64 (12). Found: *m/z* 227.0459. Calcd for $C_{10}H_{13}NOS_2$: M, 227.0439.

**Methyl *N*-Methyl-*N*-(4-nitrophenyl)dithiocarbamate (2g).** Yield: 79%. A brown powder, mp 128.5—129.4 °C; $R_f$ = 0.40 (hexane : EtOAc = 5 : 1). IR (KBr) 3098, 3062, 2910, 1606, 1590, 1523, 1486, 1462, 1430, 1340, 1308, 1290, 1260, 1094, 1010, 957, 860, 800, 694 cm$^{-1}$; $^1$H NMR (90 MHz) $\delta$ = 2.57 (s, 3 H), 3.77 (s, 3 H), 7.47 (d, $J$ = 9 Hz, 2 H), 8.32 (d, $J$ = 9 Hz, 2 H); $^{13}$C NMR (75.5 MHz) $\delta$ = 20.1 (s), 45.2 (s), 125.1 (s), 128.3 (s), 147.3 (s), 150.3 (s), 200.5 (s); MS *m/z* (rel intensity) 243 ($M^+$+1; 7), 242 ($M^+$; 58), 196 (16), 195 (100), 150 (15), 149 (40), 134 (18), 93 (12), 92 (5), 91 (92), 88 (69), 77 (21), 75 (16), 74 (19), 64 (14), 63 (24). Found: *m/z* 242.0171. Calcd for $C_9H_{10}N_2O_2S_2$: M, 242.0184.

**Methyl 2,3-Dihydro-1-indolyldithiocarbamate (2h).** Yield: 92%. A white powder, mp 86.8—87.4 °C; $R_f$ = 0.45 (hexane : EtOAc = 10 : 1). IR (KBr) 3108, 3043, 2940, 2928, 2910, 1477, 1458, 1396, 1350, 1318, 1296, 1252, 1218, 1165, 1100, 1060, 1021, 970, 948, 783, 760, 702 cm$^{-1}$; $^1$H NMR (90 MHz) $\delta$ = 2.71 (s, 3 H), 3.20 (t, $J$ = 8 Hz, 2 H), 4.51 (t, $J$ = 8 Hz, 2 H), 7.1—7.3 (m, 3 H), 9.0—9.2 (br s, 1 H); $^{13}$C NMR (75.5 MHz) $\delta$ = 19.5 (s), 27.3 (s), 54.5 (m), 118.4 (s), 125.1 (s), 125.2 (s), 126.7 (s), 134.4 (s), 144.0 (m), 193.4 (s); MS *m/z* (rel intensity) 211 ($M^+$+2; 6), 210 ($M^+$+1; 7), 209 ($M^+$; 66), 163 (10), 162 (88), 129 (13), 128 (100), 118 (29), 91 (70), 89 (15), 77 (37), 74 (32), 69 (13), 65 (15), 63 (13). Found: *m/z* 209.0347. Calcd for $C_{10}H_{11}NS_2$: M, 209.0333.

**Methyl *N*,*N*-Di(3-methylphenyl)dithiocarbamate (2i).** Yield: 82%. Orange crystals, mp 103.1—104.2 °C; $R_f$ = 0.44 (hexane : EtOAc = 10 : 1). IR (KBr) 2919, 1603, 1584, 1356, 1287, 1184, 1055, 1003, 949, 772, 745 cm$^{-1}$; $^1$H NMR (90 MHz) $\delta$ = 2.30 (s, 6 H), 2.53 (s, 3 H), 7.0—7.3 (m, 8 H); $^{13}$C NMR (75.5 MHz) $\delta$ = 20.8 (s), 21.3 (s), 124.8 (s), 128.3 (s), 129.0 (s), 129.2 (s), 140.0 (s), 145.1 (m), 202.7 (s); MS *m/z* (rel intensity) 289 ($M^+$+2; 3), 288 ($M^+$+1; 18), 287 ($M^+$; 12), 286 ($M^+$−1; 19), 240 (16), 222 (23), 207 (33), 180 (13), 179 (14), 178 (23), 164 (100), 149 (26), 145 (19), 143 (47), 123 (17), 109 (19), 108 (31), 97 (32), 91 (46), 83 (36), 71 (33), 69 (36), 65 (35). Found: *m/z* 287.0804. Calcd for $C_{16}H_{17}NS_2$: M, 287.0802.

**Methyl *N*-(4-Bromo-2-fluorophenyl)-*N*-methyldithiocarbamate (2j).** Yield: 90%. A colorless solid, mp 74.5—74.7 °C (EtOH); $R_f$ = 0.65 (hexane : $Et_2O$ = 10 : 1). IR (KBr) 3031, 2924, 1595, 1576, 1489, 1404, 1364, 1312, 1211, 1098, 1063, 954, 874, 822, 779, 727 cm$^{-1}$; $^1$H NMR (200 MHz) $\delta$ = 2.57 (s, 3 H), 3.70 (s, 3 H), 7.14—7.26 (m, 1 H), 7.35—7.43 (m, 2 H); $^{19}$F NMR (188 MHz) $\delta$ = −117.47 (m); $^{13}$C NMR (50.3 MHz) $\delta$ = 20.6 (s), 44.7 (s), 120.8 (d, $J$ = 23 Hz), 123.4 (m), 130.4 (br), 130.8 (m), 157.0 (d, $^1J_{C-F}$ = 257 Hz), 201.5 (s); MS *m/z* (rel intensity) 297 ($M^+$+2; 28), 295 ($M^+$; 25), 248 (40), 246 (41), 233 (39), 231 (38), 214 (17), 167 (19), 152 (14), 108 (22), 94 (26), 91 (56), 88 (100), 74 (12). Found: C, 36.94; H, 3.00; N, 4.82%. Calcd for $C_9H_9BrFNS_2$: C, 36.74; H, 3.08; N, 4.76%.

**Methyl *N*-(4-Bromo-2-fluorophenyl)-*N*-ethyldithiocarbamate (2k).** Yield: 87%. A pale brown oil, bp 210 °C/0.8 mmHg; $R_f$ = 0.50 (hexane : $Et_2O$ = 10 : 1). IR 2977, 1891, 1528, 1491, 1271, 1136, 912, 866, 808 cm$^{-1}$; $^1$H NMR (200 MHz) $\delta$ = 1.24 (t, $J$ = 7 Hz, 3 H), 2.55 (s, 3 H), 3.95—4.27 (m, 1 H), 4.27—4.60 (m, 1 H), 7.08—7.16 (m, 1 H), 7.36—7.44 (m, 2 H); $^{19}$F NMR (188 MHz) $\delta$ = −116.41 (m); $^{13}$C NMR (50.3 MHz) $\delta$ = 11.6 (s), 20.2 (s), 51.4 (s), 120.6 (d, $J$ = 23 Hz), 123.4 (m), 129.0 (m), 131.2 (br s), 157.2 (d, $^1J_{C-F}$ = 257 Hz), 200.7 (s); MS *m/z* (rel intensity) 310 ($M^+$+3; 4), 309 ($M^+$+2; 37), 308 ($M^+$+1; 3), 307 ($M^+$; 33), 290 (6), 288 (6), 262 (20), 260 (20), 234 (71), 233 (23), 232 (70), 231 (17), 216 (26), 153 (60), 152 (21), 137 (22), 133 (21), 108 (40), 102 (100), 94 (54), 91 (71). Found: C, 38.82; H, 3.60; N, 4.49%. Calcd for $C_{10}H_{11}BrFNS_2$: C, 38.97; H, 3.60; N, 4.54%.

**Methyl *N*-(4-Bromo-2-fluorophenyl)-*N*-hexyldithiocarbamate (2l).** Yield: 74%. A dark brown oil, bp 245 °C/0.45 mmHg; $R_f$ = 0.24 (hexane). IR 2955, 2929, 1597, 1574, 1491, 1391, 1263, 1123, 1100, 1065, 878, 858, 818, 729, 610 cm$^{-1}$; $^1$H NMR (200 MHz) $\delta$ = 0.87 (t, $J$ = 7 Hz, 3 H), 1.16—1.42 (m, 6 H), 1.48—1.81 (m, 2 H), 2.55 (s, 3 H), 4.05 (m, 1 H), 4.35 (br s, 1 H), 7.07—7.16 (m, 1 H), 7.35—7.43 (m, 2 H); $^{19}$F NMR (188 MHz) $\delta$ = −116.42 (dm, $J$ = 5 Hz); $^{13}$C NMR (50.3 MHz) $\delta$ = 13.8 (s), 20.3 (s), 22.4 (s), 26.1 (s), 26.4 (br), 31.3 (s), 56.6 (s), 120.7 (d, $J$ = 23 Hz), 123.4 (m), 128.2 (d, $J$ = 4 Hz), 129.5 (m), 157.3 (d, $^1J_{C-F}$ = 257 Hz), 201.1 (s); MS *m/z* (rel intensity) 366 ($M^+$+2; 12), 364 ($M^+$; 10), 248 (16), 246 (15), 233 (25), 231 (24), 202 (13), 200 (11), 158 (39), 91 (63), 74 (32), 43 (100). Found: C, 45.82; H, 5.12; N, 3.73%. Calcd for $C_{14}H_{19}BrFNS_2$: C, 46.15; H, 5.26; N, 3.84%. Found: *m/z* 363.0130. Calcd for $C_{14}H_{19}BrFNS_2$: M, 363.0126.

**Methyl *N*-Methyl-*N*-phenyldithiocarbamate (2m).** Yield: 96%. Pale yellow crystals, mp 82.8—83.4 °C (EtOH); $R_f$ = 0.54 (hexane : EtOAc = 10 : 1). IR (KBr) 2920, 1968, 1892, 1761, 1591, 1491, 1428, 1360, 1254, 1100, 955, 772, 696, 631 cm$^{-1}$; $^1$H NMR (90 MHz) $\delta$ = 2.51 (s, 3 H), 3.78 (s, 3 H), 7.26 (m, 3 H), 7.42 (m, 2 H); $^{13}$C NMR (50.3 MHz) $\delta$ = 20.7 (s), 45.9 (s), 126.8 (s), 128.8 (s), 129.6 (s), 144.8 (s), 200.3 (s); MS *m/z* (rel intensity) 197 ($M^+$; 62), 151 (15), 150 (100), 135 (58), 109 (54), 91 (39), 88 (41). Found: C, 54.59; H, 5.44; N, 7.01%. Calcd for $C_9H_{11}NS_2$: C, 54.79; H, 5.62; N, 7.10%.

**Methyl *N*-Ethyl-*N*-phenyldithiocarbamate (2n).** Yield: 86%. Pale yellow crystals, mp 47.1—47.9 °C (EtOH); $R_f$ = 0.44 (hexane : $Et_2O$ = 10 : 1). IR (KBr) 2980, 2910, 1595, 1489, 1454, 1397, 1345, 1279, 1238, 1103, 1076, 987, 901, 762, 696, 629 cm$^{-1}$; $^1$H NMR (200 MHz) $\delta$ = 1.26 (t, $J$ = 7 Hz, 3 H), 2.52 (s, 3 H), 4.25 (q, $J$ = 7 Hz, 2 H), 7.19—7.23 (m, 2 H), 7.42—7.50 (m, 3 H); $^{13}$C NMR (50.3 MHz) $\delta$ = 11.9 (s), 20.5 (s), 52.4 (s), 128.0 (s),

129.0 (s), 129.6 (s), 143.1 (s), 199.9 (s); MS *m/z* (rel intensity) 213 ($M^+$+2; 3), 212 ($M^+$+1; 4), 211 ($M^+$; 34), 164 (21), 136 (95), 120 (42), 109 (19), 104 (17), 102 (43), 91 (35), 78 (19), 77 (100), 74 (10), 64 (10). Found: C, 56.83; H, 6.24; N, 6.68%. Calcd for $C_{10}H_{13}NS_2$: C, 56.56; H, 6.20; N, 6.63%.

**Methyl *N*-Phenyl-*N*-propyldithiocarbamate (2o).** Yield: 96%. Pale yellow crystals, mp 60.7—61.5 °C (EtOH); $R_f$ = 0.25 (hexane : $CH_2Cl_2$ = 3 : 1). IR (KBr) 2963, 2934, 2874, 1593, 1495, 1487, 1402, 1366, 1229, 1100, 953, 772, 700, 631 $cm^{-1}$; $^1H$ NMR (90 MHz) $\delta$ = 0.92 (t, $J$ = 7 Hz, 3 H), 1.74 (m, 2 H), 2.52 (s, 3 H), 4.24 (t, $J$ = 8 Hz, 2 H), 7.10—7.23 (m, 2 H), 7.42—7.67 (m, 3 H); $^{13}C$ NMR (50.3 MHz) $\delta$ = 11.0 (s), 20.0 (s), 20.6 (s), 59.1 (s), 127.9 (s), 128.9 (s), 129.6 (s), 143.4 (s), 200.4 (s); MS *m/z* (rel intensity) 226 ($M^+$+1; 5), 225 ($M^+$; 33), 178 (15), 150 (23), 136 (100), 116 (24), 91 (33), 77 (72), 51 (32), 43 (42). Found: C, 59.05; H, 6.81; N, 6.32%. Calcd for $C_{11}H_{15}NS_2$: C, 58.65; H, 6.71; N, 6.22%. Found: *m/z* 225.0646. Calcd for $C_{11}H_{15}NS_2$: M, 225.0646.

**Methyl *N*-Hexyl-*N*-phenyldithiocarbamate (2p).** Yield: 100%. A dark brown oil, bp 220 °C/0.5 mmHg; $R_f$ = 0.38 (hexane : EtOAc = 10 : 1). IR 2955, 2928, 2857, 1593, 1491, 1441, 1395, 1368, 1251, 1103, 957, 696 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta$ = 0.86 (t, $J$ = 7 Hz, 3 H), 1.11—1.42 (m, 6 H), 1.49—1.95 (m, 2 H), 2.52 (s, 3 H), 4.27 (t, $J$ = 8 Hz, 2 H), 7.15—7.26 (m, 2 H), 7.41—7.50 (m, 3 H); $^{13}C$ NMR (50.3 MHz) $\delta$ = 13.8 (s), 20.3 (s), 22.7 (s), 26.0 (s), 26.4 (s), 31.2 (s), 57.4 (s), 127.7 (s), 128.7 (s), 129.4 (s), 143.2 (s), 199.8 (s); MS *m/z* (rel intensity) 269 ($M^+$+2; 3), 267 ($M^+$; 23), 158 (21), 150 (29), 136 (99), 135 (51), 106 (48), 104 (23), 91 (94), 85 (38), 77 (100). Found: C, 62.78; H, 7.90; N, 5.19%. Calcd for $C_{14}H_{21}NS_2$: C, 62.90; H, 7.92; N, 5.24%.

**Methyl *N*-Octyl-*N*-phenyldithiocarbamate (2q).** Yield: 92%. A dark brown oil, bp 235 °C/0.6 mmHg; $R_f$ = 0.29 (hexane : $CH_2Cl_2$ = 4 : 1). IR 2926, 2855, 1593, 1491, 1395, 1368, 1248, 1103, 1073, 951, 770, 696 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta$ = 0.86 (t, $J$ = 6 Hz, 3 H), 1.08—1.43 (m, 10 H), 1.43—1.98 (m, 2 H), 2.52 (s, 3 H), 4.27 (t, $J$ = 8 Hz, 2 H), 7.17—7.42 (m, 2 H), 7.42—7.82 (m, 3 H); $^{13}C$ NMR (50.3 MHz) $\delta$ = 13.8 (s), 20.32 (s), 20.33 (s), 26.36 (s), 26.39 (s), 28.9 (s), 29.0 (s), 31.5 (s), 57.4 (s), 127.8 (s), 128.7 (s), 129.3 (s), 143.2 (s), 199.8 (s); MS *m/z* (rel intensity) 296 ($M^+$+1; 6), 295 ($M^+$; 28), 186 (17), 183 (21), 150 (50), 136 (100), 91 (55), 77 (60). Found: C, 64.96; H, 8.59; N, 4.63%. Calcd for $C_{16}H_{25}NS_2$: C, 65.03; H, 8.53; N, 4.74%.

**Methyl *N*,*N*-Dibenzyldithiocarbamate (2r).** Yield: 99%. A pale red oil; $R_f$ = 0.40 (hexane : EtOAc = 10 : 1). IR 3060, 3015, 2910, 1605, 1493, 1465, 1450, 1408, 1355, 1215, 1152, 1078, 1025, 970, 730, 690 $cm^{-1}$; $^1H$ NMR (300 MHz) $\delta$ = 2.73 (s, 3 H), 4.93 (s, 2 H), 5.37 (s, 2 H), 7.18—7.38 (m, 10 H); $^{13}C$ NMR (75.5 MHz) $\delta$ = 20.8 (s), 53.9 (s), 56.3 (s), 127.1 (s), 127.8 (s), 128.8 (s), 134.7 (m), 135.6 (m), 200.8 (s); MS *m/z* (rel intensity) 288 ($M^+$+1; 3), 287 ($M^+$; 16), 196 (22), 148 (11), 137 (34), 123 (18), 92 (11), 91 (100), 65 (30). Found: *m/z* 287.0806. Calcd for $C_{16}H_{17}NS_2$: M, 287.0802.

**Methyl *N*-Benzyl-*N*-propyldithiocarbamate (2s).** Yield: 96%. A pale red oil; $R_f$ = 0.49 (hexane : EtOAc = 10 : 1). IR 2965, 2930, 2917, 2874, 1605, 1495, 1476, 1455, 1435, 1410, 1381, 1302, 1231, 1188, 1121, 1078, 1030, 1001, 958, 731, 698 $cm^{-1}$; $^1H$ NMR (300 MHz) $\delta$ = 0.90 (t, $J$ = 8 Hz, 3 H), 1.65—1.80 (m, 2 H), 2.60—2.75 (m, 3 H), 3.45—3.65 (m, 1 H), 3.85—4.00 (m, 1 H), 4.97 (br s, 1 H), 5.37 (br s, 1 H), 7.20—7.70 (m, 5 H); $^{13}C$ NMR (75.5 MHz) $\delta$ = 11.1 (s), 20.1 (s), 20.2 (s), 53.0 (s), 57.1 (s), 126.7 (s), 127.4 (s), 128.5 (s), 135.8 (m), 199.4 (s); MS *m/z* (rel intensity) 240 ($M^+$+1; 1), 239 ($M^+$; 11), 149 (5), 148 (8), 91 (100), 74 (6), 65 (12). Found: *m/z* 239.0802. Calcd for $C_{12}H_{17}NS_2$: M, 239.0824.

**Methyl *N*-Methyl-*N*-(2-pyridyl)dithiocarbamate (6a).** Yield: 96%. Colorless crystals, mp 47.5—47.7 °C; $R_f$ = 0.18 (hexane : $Et_2O$ = 2 : 1). IR (KBr) 3052, 3003, 2916, 1586, 1570, 1463, 1425, 1352, 1315, 1295, 1274, 1137, 1102, 995, 961, 791, 745, 656, 637, 621 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta$ = 2.59 (s, 3 H), 3.79 (s, 3 H), 7.32 (ddd, $J$ = 1, 5, 8 Hz, 1 H), 7.40 (ddd, $J$ = 1, 1, 8 Hz, 1 H), 7.80 (ddd, $J$ = 2, 8, 8 Hz, 1 H), 8.59 (ddd, $J$ = 1, 2, 5 Hz, 1 H); $^{13}C$ NMR (50.3 MHz) $\delta$ = 20.5 (s), 43.5 (s), 122.4 (s), 123.6 (s), 138.4 (s), 149.7 (s), 156.6 (s), 200.4 (s); MS *m/z* (rel intensity) 199 ($M^+$+1; 5), 198 ($M^+$; 46), 183 (30), 151 (40), 137 (5), 107 (19), 91 (15), 78 (100). Found: *m/z* 198.0274. Calcd for $C_8H_{10}N_2S_2$: M, 198.0285.

**Methyl *N*-Ethyl-*N*-(2-pyridyl)dithiocarbamate (6b).** Yield: 83%. A pale yellow oil; $R_f$ = 0.53 (hexane : $CH_2Cl_2$ : EtOAc = 4 : 2 : 1). IR 3052, 2975, 1586, 1466, 1433, 1389, 1348, 1273, 1111, 1013, 961, 911, 785, 745, 652 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta$ = 1.29 (t, $J$ = 7 Hz, 3 H), 2.50 (s, 3 H), 4.41 (q, $J$ = 7 Hz, 2 H), 7.30—7.38 (m, 2 H), 7.82 (ddd, $J$ = 2, 8, 8 Hz, 1 H), 8.62 (dd, $J$ = 2, 5 Hz, 1 H); $^{13}C$ NMR (50.3 MHz) $\delta$ = 12.3 (s), 20.3 (s), 50.8 (s), 123.6 (s), 123.9 (s), 138.4 (s), 150.0 (s), 155.5 (s), 199.8 (s); MS *m/z* (rel intensity) 214 ($M^+$+2; 6), 213 ($M^+$+1; 8), 212 ($M^+$; 53), 197 (22), 165 (22), 137 (94), 121 (100), 91 (35), 79 (41), 78 (96). Found: C, 50.84; H, 5.48; N, 13.01%. Calcd for $C_9H_{12}N_2S_2$: C, 50.91; H, 5.70; N, 13.19%.

**Methyl *N*-Hexyl-*N*-(2-pyridyl)dithiocarbamate (6c).** Yield: 88%. A dark red oil; $R_f$ = 0.69 (hexane : $Et_2O$ = 4 : 1). IR 2956, 2928, 2857, 1587, 1465, 1432, 1391, 1366, 1264, 1111, 995, 745 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta$ = 0.85 (t, $J$ = 7 Hz, 3 H), 1.13—1.41 (m, 6 H), 1.60—1.81 (m, 2 H), 2.57 (s, 3 H), 4.25—4.40 (m, 2 H), 7.28—7.41 (m, 2 H), 7.80 (ddd, $J$ = 2, 8, 8 Hz, 1 H), 8.60 (dd, $J$ = 2, 5 Hz, 1 H); $^{13}C$ NMR (50.3 MHz) $\delta$ = 13.9 (s), 20.2 (s), 22.5 (s), 26.3 (s), 26.9 (s), 31.4 (s), 55.8 (s), 123.5 (s), 123.7 (s), 138.2 (s), 149.9 (s), 155.8 (s), 200.0 (s); MS *m/z* (rel intensity) 269 ($M^+$+1; 6), 268 ($M^+$; 35), 253 (14), 183 (4), 177 (78), 137 (100), 107 (11), 91 (26), 78 (50). Found: *m/z* 268.1066. Calcd for $C_{13}H_{20}N_2S_2$: M, 268.1068.

**Methyl *N*-Octyl-*N*-(2-pyridyl)dithiocarbamate (6d).** Yield: 93%. A pale yellow oil; $R_f$ = 0.27 (hexane : $Et_2O$ = 5 : 1). IR 3055, 2954, 2917, 2868, 2847, 1583, 1465, 1453, 1432, 1397, 1368, 1300, 1273, 1263, 1226, 1146, 1110, 1093, 994, 747, 634 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta$ = 0.85 (t, $J$ = 7 Hz, 3 H), 1.16—1.25 (m, 10 H), 1.67—1.71 (m, 2 H), 2.57 (s, 3 H), 4.29—4.37 (m, 2 H), 7.28—7.45 (m, 2 H), 7.80 (ddd, $J$ = 2, 2, 8 Hz, 1 H), 8.60 (dd, $J$ = 2, 5 Hz, 1 H); $^{13}C$ NMR (50.3 MHz) $\delta$ = 14.0 (s), 20.2 (s), 22.6 (s), 26.7 (s), 26.9 (s), 29.1 (s), 29.2 (s), 31.7 (s), 55.8 (s), 123.5 (s), 123.7 (s), 138.2 (s), 149.9 (s), 155.9 (s), 200.0 (s); MS *m/z* (rel intensity) 297 ($M^+$+1; 5), 296 ($M^+$; 30), 281 (16), 249 (10), 205 (84), 137 (100), 91 (25), 78 (45). Found: *m/z* 296.1376. Calcd for $C_{15}H_{24}N_2S_2$: M, 296.1381.

**Methyl *N*-Dodecyl-*N*-(2-pyridyl)dithiocarbamate (6e).** Yield: 93%. A yellow powder, mp 54.8—55.3 °C; $R_f$ = 0.40 (hexane : $Et_2O$ = 5 : 2). IR (KBr) 2955, 2919, 2848, 1583, 1467, 1452, 1432, 1396, 1368, 1304, 1292, 1146, 1110, 953, 745 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta$ = 0.85 (t, $J$ = 7 Hz, 3 H), 1.16—1.75 (m, 20 H), 2.57 (s, 3 H), 4.29—4.37 (m, 2 H), 7.29—7.35 (m, 2 H), 7.80 (ddd, $J$ = 2, 8, 8 Hz, 1 H), 8.60 (dd, $J$ = 2, 5 Hz, 1 H); $^{13}C$ NMR (50.3 MHz) $\delta$ = 14.1 (s), 20.3 (s), 22.6 (s), 26.7 (s), 27.0 (s), 29.5 (s), 31.9 (s), 55.8 (s), 123.5 (s), 123.6 (s), 138.2 (s), 149.9 (s), 155.9 (s), 200.1 (s); MS *m/z* (rel intensity) 353 ($M^+$+1; 5), 352 ($M^+$; 23), 337 (16), 262 (16), 261 (84), 137 (100), 107 (10), 78 (35). Found: *m/z* 352.2003. Calcd for $C_{19}H_{32}N_2S_2$: M, 352.2007.

**Methyl *N*-Benzyl-*N*-(2-pyridyl)dithiocarbamate (6f).** Yield:

88%. Colorless crystals, mp 86.8—87.3 °C; $R_f$ = 0.18 (hexane : $Et_2O$ = 2 : 1). IR (KBr) 3059, 3030, 2917, 1584, 1570, 1495, 1465, 1455, 1432, 1384, 1349, 1263, 1211, 1200, 1115, 996, 958, 744, 699 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta$ = 2.61 (s, 3 H), 5.68 (s, 2 H), 7.09 (ddd, $J$ = 1, 1, 8 Hz, 1 H), 7.20—7.30 (m, 6 H), 7.65 (ddd, $J$ = 2, 8, 8 Hz, 1 H), 8.59 (ddd, $J$ = 1, 2, 5 Hz, 1 H); $^{13}C$ NMR (50.3 Hz) $\delta$ = 20.7 (s), 58.8 (s), 123.8 (s), 124.2 (s), 127.6 (s), 128.4 (s), 128.5 (s), 135.9 (s), 138.0 (s), 149.9 (s), 155.3 (s), 201.4 (s); MS $m/z$ (rel intensity) 274 ($M^+$; 18), 184 (13), 183 (100), 148 (4), 137 (14), 91 (82), 78 (33). Found: $m/z$ 274.0588. Calcd for $C_{14}H_{14}N_2S_2$: M, 274.0598.

**Methyl *N*-(4-Ethylbenzyl)-*N*-(2-pyridyl)dithiocarbamate (6g).** Yield: 96%. A dark red oil; $R_f$ = 0.74 (hexane : $Et_2O$ = 3 : 1). IR 2963, 1584, 1464, 1387, 1202, 1113, 997, 969, 743 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta$ = 1.19 (t, $J$ = 8 Hz, 3 H), 2.59 (q, $J$ = 8 Hz, 2 H), 2.60 (s, 3 H), 5.64 (s, 2 H), 7.04—7.13 (m, 1 H), 7.06 (d, $J$ = 8 Hz, 2 H), 7.19 (d, $J$ = 8 Hz, 2 H), 7.22—7.31 (m, 1 H), 7.66 (ddd, $J$ = 2, 8, 8 Hz, 1 H), 8.59 (ddd, $J$ = 1, 1, 5 Hz, 1 H); $^{13}C$ NMR (50.3 MHz) $\delta$ = 15.3 (s), 20.4 (s), 28.4 (s), 58.4 (s), 123.5 (s), 124.0 (s), 127.7 (s), 128.2 (s), 132.9 (s), 137.8 (s), 143.4 (s), 149.7 (s), 155.2 (s), 201.0 (s); MS $m/z$ (rel intensity) 302 ($M^+$; 6), 211 (71), 183 (8), 137 (24), 136 (21), 121 (73), 105 (39), 91 (72), 79 (22), 78 (100), 77 (31). Found: $m/z$ 302.0905. Calcd for $C_{16}H_{18}N_2S_2$: M, 302.0911.

**Methyl *N*-Benzyl-*N*-(3-pyridyl)dithiocarbamate (6h).** Yield: 93%. Colorless crystals, mp 113.9—114.4 °C; $R_f$ = 0.55 (hexane : $Et_2O$ = 1 : 4). IR (KBr) 3062, 2911, 1494, 1475, 1430, 1419, 1388, 1351, 1266, 1220, 1191, 1112, 985, 963, 957, 734, 708, 699 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta$ = 2.58 (s, 3 H), 5.59 (s, 2 H), 7.25—7.32 (m, 7 H), 8.32 (dd, $J$ = 1, 2 Hz, 1 H), 8.58 (dd, $J$ = 2, 5 Hz, 1 H); $^{13}C$ NMR (50.3 MHz) $\delta$ = 21.1 (s), 60.4 (s), 123.9 (s), 128.1 (s), 128.7 (s), 128.8 (s), 135.3 (s), 136.0 (s), 139.5 (s), 149.5 (s), 149.9 (s), 202.4 (s); MS $m/z$ (rel intensity) 274 ($M^+$; 20), 227 (7), 183 (7), 151 (5), 137 (5), 136 (5), 109 (21), 108 (78), 91 (100), 78 (11). Found: $m/z$ 274.0590. Calcd for $C_{14}H_{14}N_2S_2$: M, 274.0598.

**Methyl *N*-Methyl-*N*-(2-pyrimidyl)dithiocarbamate (10a).** Yield: 76%. An orange powder, mp 61.5—62.1 °C; $R_f$ = 0.40 (hexane : $Et_2O$ = 1 : 2). IR (KBr) 1567, 1445, 1425, 1397, 1341, 1315, 1252, 1155, 1108, 810 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta$ = 2.62 (s, 3 H), 3.97 (s, 3 H), 7.22 (t, $J$ = 5 Hz, 1 H), 8.78 (d, $J$ = 5 Hz, 2 H); $^{13}C$ NMR (50.3 MHz) $\delta$ = 21.4 (s), 42.9 (s), 118.6 (s), 158.2 (s), 161.4 (s), 202.4 (s); MS $m/z$ (rel intensity) 201 ($M^+$+2; 6), 200 ($M^+$+1; 7), 199 ($M^+$; 69), 184 (16), 152 (100), 108 (22), 91 (19), 79 (81). Found: $m/z$ 199.0232. Calcd for $C_7H_9N_3S_2$: M, 199.0238.

**Methyl *N*-Propyl-*N*-(2-pyrimidyl)dithiocarbamate (10b).** Yield: 82%. A pale red oil; $R_f$ = 0.41 (hexane : $Et_2O$ = 1 : 2). IR 2965, 2932, 2874, 1566, 1462, 1406, 1366, 1294, 1283, 1148, 1119, 1073, 959, 814 $cm^{-1}$; $^1H$ NMR (300 MHz) $\delta$ = 0.92 (t, $J$ = 8 Hz, 3 H), 1.78 (sextet, $J$ = 8 Hz, 2 H), 4.51 (tm, $J$ = 8 Hz, 2 H), 7.27 (t, $J$ = 5 Hz, 1 H), 8.80 (d, $J$ = 5 Hz, 2 H); $^{13}C$ NMR (75.5 MHz) $\delta$ = 11.0 (s), 20.5 (s), 20.8 (s), 56.4 (s), 119.0 (s), 158.4 (s), 161.2 (s), 201.5 (s); MS $m/z$ (rel intensity) 229 ($M^+$+2; 3), 228 ($M^+$+1; 3), 227 ($M^+$; 28), 212 (7), 180 (10), 138 (100), 136 (33), 91 (23), 79 (56). Found: $m/z$ 227.0552. Calcd for $C_9H_{13}N_3S_2$: M, 227.0551.

**Methyl *N*-Hexyl-*N*-(2-pyrimidyl)dithiocarbamate (10c).** Yield: 77%. A pale yellow oil; $R_f$ = 0.38 (hexane : EtOAc = 3 : 1). IR 2955, 2928, 2857, 1564, 1408, 1381, 1294, 1249, 1191, 1145, 1120, 1073, 994, 955, 808, 671 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta$ = 0.85 (t, $J$ = 7 Hz, 3 H), 1.20—1.38 (m, 6 H), 1.72—1.80 (m, 2 H), 2.61 (s, 3 H), 4.53 (t, $J$ = 8 Hz, 2 H), 7.24 (t, $J$ = 5 Hz, 1 H), 8.79 (d, $J$ = 5 Hz, 2 H); $^{13}C$ NMR (50.3 MHz) $\delta$ = 14.0 (s), 20.9 (s), 22.5 (s), 26.3 (s), 27.2 (s), 31.3 (s), 55.0 (s), 119.1 (s), 158.4 (s), 161.4 (s), 201.5 (s); MS $m/z$ (rel intensity) 270 ($M^+$+1; 5), 269 ($M^+$; 35), 254 (8), 222 (14), 178 (31), 138 (100), 108 (16), 79 (30). Found: $m/z$ 269.1023. Calcd for $C_{12}H_{19}N_3S_2$: M, 269.1020.

**Methyl *N*-Octyl-*N*-(2-pyrimidyl)dithiocarbamate (10d).** Yield: 75%. A pale yellow oil; $R_f$ = 0.26 (hexane : EtOAc = 3 : 1). IR 2955, 2925, 2855, 1564, 1407, 1381, 1367, 1295, 1272, 1230, 1176, 1143, 1120, 1090, 1072, 954, 808, 671, 640 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta$ = 0.86 (t, $J$ = 6 Hz, 3 H), 1.17—1.26 (m, 10 H), 1.69—1.80 (m, 2 H), 2.61 (s, 3 H), 4.49—4.57 (m, 2 H), 7.23 (t, $J$ = 5 Hz, 1 H), 8.79 (d, $J$ = 5 Hz, 2 H); $^{13}C$ NMR (50.3 MHz) $\delta$ = 14.0 (s), 20.9 (s), 22.5 (s), 26.6 (s), 27.2 (s), 29.1 (s), 29.1 (s), 31.7 (s), 55.0 (s), 119.1 (s), 158.4 (s), 161.4 (s), 201.4 (s); MS $m/z$ (rel intensity) 298 ($M^+$+1; 6), 297 ($M^+$; 31), 282 (11), 250 (17), 206 (33), 138 (100), 108 (17), 91 (26), 79 (27). Found: $m/z$ 297.1343. Calcd for $C_{14}H_{23}N_3S_2$: M, 297.1333.

**Methyl *N*-Dodecyl-*N*-(2-pyrimidyl)dithiocarbamate (10e).** Yield: 57%. A pale yellow oil; $R_f$ = 0.32 (hexane : $Et_2O$ = 3 : 1). IR 2957, 2920, 2849, 1577, 1564, 1406, 1376, 1366, 1296, 1226, 1153, 1112, 953, 804 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta$ = 0.87 (t, $J$ = 6 Hz, 3 H), 1.24—1.40 (m, 18 H), 1.65—1.88 (m, 2 H), 2.61 (s, 3 H), 4.49—4.57 (m, 2 H), 7.22 (t, $J$ = 5 Hz, 1 H), 8.78 (d, $J$ = 5 Hz, 1 H); $^{13}C$ NMR (75.5 Hz) $\delta$ = 14.0 (s), 20.8 (s), 22.6 (s), 26.6 (s), 27.1 (s), 29.1 (s), 29.2 (s), 29.37 (s), 29.42 (s), 29.5 (s), 31.8 (s), 54.9 (s), 119.0 (s), 158.3 (s), 161.2 (s), 201.3 (s); MS $m/z$ (rel intensity) 354 ($M^+$+1; 5), 353 ($M^+$; 24), 338 (10), 306 (18), 262 (30), 138 (100), 108 (14), 91 (23), 79 (20). Found: $m/z$ 353.1958. Calcd for $C_{18}H_{31}N_3S_2$: M, 353.1959.

**A General Procedure for the Preparation of Trifluoromethylamines:** To a stirred solution of $TBAH_2F_3$ (10 mmol) and a dithiocarbamate (2.0 mmol) in $CH_2Cl_2$ (4.0 mL) was added an *N*-halo imide (see Table 1, 8.0 mmol) in one portion at room temperature. The resulting mixture was stirred for 1 h at room temperature, then poured into an aq. solution of $NaHCO_3$, NaOH and $NaHSO_3$ and extracted with diethyl ether three times. The combined organic phase was dried over anhydrous sodium sulfate, filtered through a pad of Celite/silica gel (Wako Gel C-100), and concentrated. The residue was purified by column chromatography or bulb-to-bulb distillation to give the desired trifluoromethylamine. The yields (*N*-halo imide) and spectroscopic properties of the products are given below.

**Diphenyl(trifluoromethyl)amine (3a).** Yield: 78% (NBS). A colorless oil; $R_f$ = 0.74 (hexane : benzene = 4 : 1). IR 3068, 3045, 2960, 2925, 1950, 1872, 1800, 1720, 1591, 1494, 1452, 1382, 1318, 1299, 1270, 1201, 1096, 1074, 1032, 1001, 950, 921, 904, 771, 754, 740, 696 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta$ = 7.2—7.3 (m, 6 H), 7.3—7.4 (m, 4 H); $^{19}F$ NMR (188 MHz) $\delta$ = −54.77 (s); $^{13}C$ NMR (75.5 MHz) $\delta$ = 121.8 (q, $^1J_{C-F}$ = 256 Hz), 126.0 (q, $J$ = 2 Hz), 126.4 (s), 129.2 (s), 141.5 (s); MS $m/z$ (rel intensity) 239 ($M^+$+2; 1), 238 ($M^+$+1; 14), 237 ($M^+$; 100), 236 (39), 235 (3), 218 (7), 216 (7), 169 (4), 168 (34), 167 (65), 166 (11). Found: $m/z$ 237.0769. Calcd for $C_{13}H_{10}F_3N$: M, 237.0765.

**Benzyl(4-methoxyphenyl)(trifluoromethyl)amine (3b).** Yield: 99% (NBS). A pale yellow oil; $R_f$ = 0.74 (hexane : $Et_2O$ = 10 : 1). IR 3090, 3062, 3000, 2928, 1720, 1608, 1581, 1511, 1454, 1440, 1380, 1291, 1248, 1223, 1180, 1167, 1100, 1078, 1052, 1034, 990, 908, 836, 734, 698 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta$ = 3.77 (s, 3 H), 4.47 (s, 2 H), 6.79 (d, $J$ = 9 Hz, 2 H), 7.13 (d, $J$ = 9 Hz, 2 H), 7.2—7.3 (m, 5 H); $^{19}F$ NMR (188 MHz) $\delta$ = −58.74 (s); $^{13}C$ NMR (75.5 MHz) $\delta$ = 53.5 (q, $J$ = 1 Hz), 55.2 (s), 114.1 (s), 123.7 (q, $^1J_{C-F}$ = 255 Hz), 127.4 (s), 128.3 (s), 128.8 (s), 129.2 (m), 133.5 (s), 136.9 (s), 158.4 (s); MS $m/z$ (rel intensity) 282 ($M^+$+1; 6), 281 ($M^+$; 34), 204 (3), 190 (8), 126 (2), 92 (8), 91 (100). Found: $m/z$ 281.1024. Calcd for $C_{15}H_{14}F_3ON$: M, 281.1027.

**Benzyl(4-chlorophenyl)(trifluoromethyl)amine (3c).** Yield: 88% (NBS). A colorless oil; $R_f = 0.74$ (hexane : $Et_2O = 10 : 1$). IR 3092, 3071, 3038, 2927, 1977, 1952, 1897, 1721, 1652, 1600, 1496, 1454, 1374, 1310, 1258, 1229, 1189, 1098, 1054, 1017, 996, 908, 837, 724, 698 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta = 4.52$ (s, 2 H), 7.09 (d, $J = 9$ Hz, 2 H), 7.23 (d, $J = 9$ Hz, 2 H), 7.3—7.4 (m, 5 H); $^{19}F$ NMR (188 MHz) $\delta = -58.20$ (s); $^{13}C$ NMR (50.3 MHz) $\delta = 53.2$ (q, $J = 1$ Hz), 123.2 (q, $^1J_{C-F} = 256$ Hz), 127.3 (q, $J = 2$ Hz), 127.6 (s), 127.9 (s), 128.5 (s), 129.2 (s), 132.1 (s), 136.4 (s), 139.5 (s); MS *m/z* (rel intensity) 288 ($M^+$+3; 0.3), 287 ($M^+$+2; 3), 286 ($M^+$+1; 1), 285 ($M^+$; 9), 92 (8), 91 (100). Found: *m/z* 285.0534. Calcd for $C_{14}H_{11}ClF_3N$: M, 285.0532.

**Benzyl(4-fluorophenyl)(trifluoromethyl)amine (3d).** Yield: 84% (NBS). A colorless oil; $R_f = 0.70$ (hexane : $Et_2O = 10 : 1$). IR 3090, 3070, 3035, 2925, 2878, 1900, 1892, 1769, 1721, 1608, 1510, 1452, 1378, 1310, 1260, 1220, 1182, 1157, 1100, 1078, 1054, 991, 840, 820, 758, 728, 699 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta = 4.50$ (s, 2 H), 6.96 (dd, $J = 9$, 9 Hz, 2 H), 7.16 (dd, $J = 5$, 9 Hz, 2 H), 7.2—7.4 (m, 5 H); $^{19}F$ NMR (188 MHz) $\delta = -58.68$ (s, 3 F), −115.26 (dd, $J = 5$, 9 Hz, 1 F); $^{13}C$ NMR (50.3 MHz) $\delta = 53.5$ (q, $J = 1$ Hz), 115.9 (q, $J = 23$ Hz), 123.4 (q, $^1J_{C-F} = 256$ Hz), 127.6 (s), 128.2 (s), 128.4 (s), 128.9 (dd, $J = 2$, 9 Hz), 136.5 (s), 136.7 (d, $J = 3$ Hz), 161.3 (d, $^1J_{C-F} = 247$ Hz); MS *m/z* (rel intensity) 270 ($M^+$+1; 1), 269 ($M^+$; 7), 92 (8), 91 (100). Found: *m/z* 269.0831. Calcd for $C_{14}H_{11}F_4N$: M, 269.0828.

**Benzyl(4-cyanophenyl)(trifluoromethyl)amine (3e).** Yield: 78% (NBS), 99% (DBH). A pale yellow oil; $R_f = 0.72$ (hexane : $Et_2O = 2 : 1$). IR 3092, 3064, 3032, 2928, 2224, 1720, 1608, 1515, 1452, 1378, 1332, 1296, 1260, 1224, 1194, 1108, 1080, 1060, 1000, 834, 736, 697 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta = 4.71$ (s, 2 H), 7.19 (d, $J = 9$ Hz, 2 H), 7.2—7.4 (m, 5 H), 7.55 (d, $J = 9$ Hz, 2 H); $^{19}F$ NMR (188 MHz) $\delta = -56.90$ (s); $^{13}C$ NMR (75.5 MHz) $\delta = 52.1$ (s), 107.7 (s), 118.4 (s), 121.9 (s), 122.5 (q, $^1J_{C-F} = 258.1$ Hz), 126.7 (s), 127.7 (s), 128.9 (s), 133.1 (s), 136.0 (s), 145.1 (s); MS *m/z* (rel intensity) 277 ($M^+$+1; 1), 276 ($M^+$; 3), 92 (8), 91 (100). Found: *m/z* 276.0879. Calcd for $C_{15}H_{10}F_3N_2$: M, 276.0874. This compound was prepared alternatively in 97% or 99% yield by treatment with 70% HF/pyridine or $(HF)_3/Et_3N$ (2.0 mL) and NBS (8.0 mmol) at 0 °C for 1 h, respectively.

**4-Methoxyphenyl(methyl)(trifluoromethyl)amine (3f).** Yield: 90% (NBS). A colorless oil; $R_f = 0.64$ (hexane : $Et_2O = 10 : 1$). IR 2960, 2940, 2910, 2842, 1516, 1474, 1437, 1339, 1271, 1250, 1196, 1146, 1055, 835 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta = 2.98$ (q, $J = 1$ Hz, 3 H), 3.81 (s, 3 H), 6.88 (d, $J = 9$ Hz, 2 H), 7.23 (d, $J = 9$ Hz, 2 H); $^{19}F$ NMR (188 MHz) $\delta = -61.98$ (s); $^{13}C$ NMR (75.5 MHz) $\delta = 36.8$ (q, $J = 2$ Hz), 55.4 (s), 114.3 (s), 123.7 (q, $^1J_{C-F} = 255$ Hz), 127.4 (s), 135.6 (s), 158.2 (s); MS *m/z* (rel intensity) 206 ($M^+$+1; 9), 205 ($M^+$; 80), 191 (9), 190 (100), 186 (8), 162 (33), 92 (10), 83 (16), 77 (13), 69 (18), 65 (34). Found: *m/z* 205.0716. Calcd for $C_9H_{10}F_3ON$: M, 205.0714.

**Methyl(4-nitrophenyl)(trifluoromethyl)amine (3g).** Yield: 68% (NBS), 96% (DBH). A pale yellow oil; $R_f = 0.46$ (hexane : $Et_2O = 5 : 1$). IR 3120, 3085, 2928, 2850, 1720, 1601, 1518, 1478, 1441, 1380, 1334, 1263, 1201, 1141, 1100, 1062, 901, 849, 751, 731, 692 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta = 3.19$ (q, $J = 1$ Hz, 3 H), 7.26 (d, $J = 9$ Hz, 2 H), 8.21 (d, $J = 9$ Hz, 2 H); $^{19}F$ NMR (188 MHz) $\delta = -58.88$ (s); $^{13}C$ NMR (75.5 MHz) $\delta = 35.1$ (q, $J = 2$ Hz), 120.8 (q, $J = 2$ Hz), 122.3 (q, $^1J_{C-F} = 258$ Hz), 124.8 (s), 143.6 (s), 147.9 (s); MS *m/z* (rel intensity) 221 ($M^+$+1; 10), 220 ($M^+$; 100), 201 (13), 190 (41), 162 (17), 159 (23). Found: *m/z* 220.0456. Calcd for $C_8H_7F_3O_2N_2$: M, 220.0460.

**1-Trifluoromethyl-2,3-dihydroindole (3h).** Yield: 76% (NBS). A colorless oil; $R_f = 0.72$ (hexane : $Et_2O = 10 : 1$). IR 3074, 3050, 3035, 2992, 2954, 2918, 2885, 2851, 1794, 1720, 1602, 1483, 1440, 1374, 1339, 1318, 1301, 1270, 1242, 1200, 1180, 1169, 1120, 1090, 1058, 951, 874, 809, 750, 720, 682 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta = 3.11$ (t, $J = 8$ Hz, 2 H), 3.73 (t, $J = 8$ Hz, 2 H), 6.9—7.2 (m, 2 H), 7.2—7.4 (m, 2 H); $^{19}F$ NMR (188 MHz) $\delta = -61.74$ (s); $^{13}C$ NMR (75.5 MHz) $\delta = 28.5$ (s), 47.9 (q, $J = 2$ Hz), 112.2 (q, $J = 3$ Hz), 122.4 (s), 122.9 (q, $^1J_{C-F} = 257$ Hz), 125.0 (s), 127.6 (s), 130.4 (s), 143.2 (s); MS *m/z* (rel intensity) 187 ($M^+$; 23), 186 ($M^+-1$; 41), 185 (37), 117 (45), 155 (11), 97 (11), 95 (12), 92 (11), 90 (17), 89 (31), 81 (16), 71 (30), 69 (100), 63 (43). Found: *m/z* 187.0602. Calcd for $C_9H_8F_3N$: M, 187.0609.

**Bis(3-methylphenyl)(trifluoromethyl)amine (3i).** Yield: 48% (NBS), 74% (NIS). A colorless oil; $R_f = 0.70$ (hexane : $Et_2O = 10 : 1$). IR 3038, 2952, 2924, 2858, 1720, 1603, 1583, 1491, 1450, 1380, 1310, 1299, 1269, 1247, 1209, 1153, 1082, 961, 904, 853, 840, 787, 695 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta = 2.36$ (s, 6 H), 7.0—7.1 (m, 6 H), 7.2—7.3 (m, 2 H); $^{19}F$ NMR (188 MHz) $\delta = -54.51$ (s); $^{13}C$ NMR (75.5 MHz) $\delta = 21.4$ (s), 121.9 (q, $^1J_{C-F} = 257$ Hz), 123.1 (s), 126.7 (s), 126.9 (s), 128.9 (s), 139.2 (s), 141.5 (s); MS *m/z* (rel intensity) 266 ($M^+$+1; 17), 265 ($M^+$; 100), 264 ($M^+-1$; 12), 251 (2), 250 (15), 133 (19), 132 (12). Found: *m/z* 265.1073. Calcd for $C_{15}H_{14}F_3N$: M, 265.1078.

***N*-Methyl-*N*-trifluoromethyl-4-bromo-2-fluoroaniline (3j).** Yield: 87% (DBH). A colorless oil, bp 118 °C/10 mmHg; $R_f = 0.57$ (hexane). IR 2960, 1578, 1499, 1347, 1296, 1225, 1150, 1090, 1076, 1057, 907, 858, 820 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta = 3.00$ (q, $J = 1$ Hz, 3 H), 7.16—7.33 (m, 3 H); $^{19}F$ NMR (188 MHz) $\delta = -61.55$ (s, 3 F), −117.62 (m, 1 F); $^{13}C$ NMR (50.3 MHz) $\delta = 35.9$ (s), 119.6 (s), 120.5 (d, $J = 24$ Hz), 121.0 (d, $J = 9$ Hz), 122.9 (q, $^1J_{C-F} = 256$ Hz), 127.8 (d, $J = 1$ Hz), 129.6 (m), 158.8 (dm, $^1J_{C-F} = 256$ Hz); MS *m/z* (rel intensity) 274 ($M^+$+3; 9), 273 ($M^+$+2; 100), 271 ($M^+$; 94), 270 (48), 252 (11), 204 (17), 203 (17), 202 (29), 201 (19), 177 (42), 157 (15), 155 (13), 123 (24), 122 (17), 108 (19), 103 (15), 95 (15), 94 (33), 81 (16), 75 (21), 69 (39). Found: C, 37.82; H, 2.57; N, 5.22%. Calcd for $C_8H_7BrF_3N$: C, 37.82; H, 2.78; N, 5.51%.

***N*-Ethyl-*N*-trifluoromethyl-4-bromo-2-fluoroaniline (3k).** Yield: 82% (DBH). A colorless oil, bp 85 °C/10 mmHg; $R_f = 0.56$ (hexane). IR 2988, 1578, 1499, 1408, 1352, 1271, 1242, 1223, 1146, 1074, 920, 860, 820 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta = 1.07$ (t, $J = 7$ Hz, 3 H), 3.38 (q, $J = 7$ Hz, 3 H), 7.15—7.34 (m, 3 H); $^{19}F$ NMR (188 MHz) $\delta = -58.60$ (s, 3 F), −117.04 (m, 1 F); $^{13}C$ NMR (50.3 MHz) $\delta = 13.4$ (s), 43.2 (q, $J = 1$ Hz), 120.4 (d, $J = 24$ Hz), 121.5 (d, $J = 27$ Hz), 123.0 (q, $^1J_{C-F} = 265$ Hz), 126.9 (d, $J = 12$ Hz), 127.8 (d, $J = 4$ Hz), 131.5 (qm, $J = 1$ Hz), 159.7 (dd, $J = 1$ Hz, $^1J_{C-F} = 256$ Hz); MS *m/z* (rel intensity) 288 ($M^+$+3; 6), 287 ($M^+$+2; 37), 286 ($M^+$+1; 7), 285 ($M^+$; 42), 273 (11), 272 (89), 271 (13), 270 (100), 257 (9), 240 (9), 239 (20), 237 (20), 203 (18), 201 (19), 177 (15), 108 (10), 94 (15), 69 (19). Found: C, 37.48; H, 2.76; N, 4.91%. Calcd for $C_9H_8BrF_3N$: C, 37.79; H, 2.82; N, 4.90%.

***N*-Hexyl-*N*-trifluoromethyl-4-bromo-2-fluoroaniline (3l).** Yield: 87% (DBH). A colorless oil, bp 110 °C/0.7 mmHg; $R_f = 0.77$ (hexane). IR 2959, 2934, 1578, 1497, 1458, 1408, 1287, 1242, 1207, 1196, 1102, 1076, 926, 860, 820, 735 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta = 0.86$ (t, $J = 6$ Hz, 3 H), 1.16—1.48 (m, 8 H), 3.29 (t, $J = 7$ Hz, 3 H), 7.19—7.34 (m, 3 H); $^{19}F$ NMR (188 MHz) $\delta = -58.90$ (s, 3 F), −116.76 (dm, $J = 12$ Hz, 1 F); $^{13}C$ NMR (50.3 MHz) $\delta = 13.9$ (s), 22.5 (s), 26.1 (s), 28.0 (s), 31.4 (s), 48.5 (q, $J = 1$ Hz), 120.3 (d, $J = 7$ Hz), 121.6 (d, $J = 9$ Hz), 122.9 (q, $^1J_{C-F} = 255$ Hz), 127.2 (d, $J = 12$ Hz), 127.9 (d, $J = 4$ Hz), 131.6 (dd, $J = 1$, 1 Hz), 159.8

(dm, $^1J_{C-F}$ = 256 Hz); MS *m/z* (rel intensity) 343 ($M^+$+3; 12), 342 ($M^+$+2; 100), 341 ($M^+$+1; 12), 340 ($M^+$; 100), 259 (37), 257 (38), 203 (29), 201 (30), 191 (31), 177 (19), 94 (37), 69 (30). Found: C, 45.98; H, 4.72; N, 4.05%. Calcd for $C_{13}H_{16}BrF_3N$: C, 45.63; H, 4.71; N, 4.09%.

***N*-Methyl-*N*-trifluoromethylaniline (3m).** Yield: 66%. A colorless oil; $R_f$ = 0.47 (hexane). IR 3067, 2984, 2923, 1601, 1497, 1476, 1437, 1333, 1269, 1196, 1148, 1090, 1059, 889, 770, 698 $cm^{-1}$; $^1H$ NMR (300 MHz) $\delta$ = 3.17 (t, *J* = 1 Hz, 3 H), 7.33—7.52 (m, 5 H); $^{19}F$ NMR (282 MHz) $\delta$ = −60.96 (s); $^{13}C$ NMR (75.5 MHz) $\delta$ = 36.3 (s), 123.4 (q, $^1J_{C-F}$ = 256 Hz), 124.9 (s), 126.1 (s), 129.1 (s), 142.8 (s); MS *m/z* (rel intensity) 176 ($M^+$+1; 9), 175 ($M^+$; 84), 174 (51), 156 (31), 106 (37), 105 (13), 104 (22), 79 (27), 78 (76), 77 (100), 74 (10), 69 (44). Found: *m/z* 175.0609. Calcd for $C_8H_8F_3N$: M, 175.0609.

***N*-Ethyl-*N*-trifluoromethylaniline (3n).** Yield: 65%. A colorless oil; $R_f$ = 0.48 (hexane). IR 2984, 2942, 1599, 1497, 1381, 1350, 1269, 1190, 1144, 1100, 1055, 909, 772, 698 $cm^{-1}$; $^1H$ NMR (300 MHz) $\delta$ = 1.08 (t, *J* = 7 Hz, 3 H), 3.42 (qq, *J* = 1, 7 Hz, 2 H), 7.23—7.39 (m, 5 H); $^{19}F$ NMR (282 MHz) $\delta$ = −58.12 (s); $^{13}C$ NMR (75.5 MHz) $\delta$ = 13.7 (s), 43.8 (s), 123.5 (q, $^1J_{C-F}$ = 256 Hz), 126.6 (s), 126.8 (q, *J* = 2 Hz), 129.1 (s), 140.7 (S); MS *m/z* (rel intensity) 189 ($M^+$; 46), 174 (100), 141 (35), 105 (24), 91 (23), 78 (38), 77 (93), 69 (39), 66 (7), 65 (27). Found: *m/z* 189.0766. Calcd for $C_9H_{10}F_3N$: M, 189.0765.

***N*-Propyl-*N*-trifluoromethylaniline (3o).** Yield: 78%. A colorless oil; $R_f$ = 0.52 (hexane). IR 2973, 2938, 2880, 1601, 1497, 1378, 1341, 1291, 1262, 1240, 1190, 1146, 1066, 932, 698 $cm^{-1}$; $^1H$ NMR (300 MHz) $\delta$ = 1.02 (t, *J* = 8 Hz, 3 H), 1.60 (sextet, *J* = 8 Hz, 2 H), 3.41 (t, *J* = 8 Hz, 2 H), 7.36—7.52 (m, 5 H); $^{19}F$ NMR (188 MHz) $\delta$ = −58.29 (s); $^{13}C$ NMR (75.5 MHz) $\delta$ = 11.1 (s), 21.4 (s), 50.8 (s), 123.5 (q, $^1J_{C-F}$ = 255 Hz), 126.7 (s), 127.0 (q, *J* = 2 Hz), 129.1 (s), 141.0 (s); MS *m/z* (rel intensity) 204 ($M^+$+1; 3), 203 ($M^+$; 25), 175 (9), 174 (100), 161 (3), 105 (12), 78 (24), 77 (59), 69 (10). Found: *m/z* 203.0922. Calcd for $C_{10}H_{12}F_3N$: M, 203.0922.

***N*-Hexyl-*N*-trifluoromethylaniline (3p).** Yield: 68%. A colorless oil; $R_f$ = 0.67 (hexane). IR 2959, 2934, 2361, 1599, 1497, 1377, 1343, 1262, 1190, 1144, 1103, 1061, 924, 698 $cm^{-1}$; $^1H$ NMR (300 MHz) $\delta$ = 0.86 (t, *J* = 7 Hz, 3 H), 1.15—1.50 (m, 8 H), 3.32 (qt, *J* = 1, 7 Hz, 2 H), 7.20—7.42 (m, 5 H); $^{19}F$ NMR (188 MHz) $\delta$ = −58.31 (s); $^{13}C$ NMR (75.5 MHz) $\delta$ = 14.0 (s), 22.5 (s), 26.2 (s), 28.1 (s), 31.3 (s), 49.0 (s), 123.5 (q, $^1J_{C-F}$ = 255 Hz), 126.7 (s), 127.0 (q, *J* = 1.2 Hz), 129.1 (s), 141.0 (s); MS *m/z* (rel intensity) 246 ($M^+$+1; 2), 245 ($M^+$; 11), 175 (11), 174 (100), 161 (12), 83 (11), 78 (11), 77 (26), 71 (17), 69 (18). Found: *m/z* 245.1388. Calcd for $C_{13}H_{18}F_3N$: M, 245.1391.

***N*-Octyl-*N*-trifluoromethylaniline (3q).** Yield: 79%. A colorless oil; $R_f$ = 0.53 (hexane). IR 2980, 2957, 2859, 1601, 1495, 1468, 1377, 1347, 1266, 1190, 1138, 1105, 1059, 907, 768, 698 $cm^{-1}$; $^1H$ NMR (300 MHz) $\delta$ = 0.87 (t, *J* = 7 Hz, 3 H), 1.15—1.35 (m, 10 H), 1.36—1.50 (m, 2 H), 3.32 (t, *J* = 7 Hz, 2 H), 7.22—7.38 (m, 5 H); $^{19}F$ NMR (188 MHz) $\delta$ = −58.29 (s); $^{13}C$ NMR (75.5 MHz) $\delta$ = 14.1 (s), 22.6 (s), 26.6 (s), 28.2 (s), 29.1 (s), 29.2 (s), 31.8 (s), 49.0 (s), 123.5 (q, $^1J_{C-F}$ = 255 Hz), 126.7 (s), 127.0 (s), 129.1 (s), 141.0 (s); MS *m/z* (rel intensity) 274 ($M^+$+1; 8), 273 ($M^+$; 15), 175 (13), 174 (100), 161 (20), 78 (10), 77 (17). Found: *m/z* 273.1699. Calcd for $C_{15}H_{22}F_3N$: M, 273.1704.

**Dibenzyl(trifluoromethyl)amine (3r).** To a stirred solution of $TBAH_2F_3$ (0.95 g, 3.2 mmol) and **2r** (0.31 g, 1.1 mmol) in dichloromethane (1.0 mL) was added NBS (0.77 g, 4.3 mmol) in one portion at room temperature. The resulting mixture was stirred for 30 min at room temperature, and diluted with a mixture of pentane and diethyl ether (5 : 1). The resulting insoluble material was filtered through a short silica gel (Wako gel C-100) column. The filtrate was concentrated under reduced pressure. The residue was purified by bulb-to-bulb distillation to give **3r** in 86% yield as a colorless oil, bp 195—205 °C/0.8 mmHg. The compound was kept in a hood, since it easily liberated hydrogen fluoride upon exposure to moisture. IR 3067, 3034, 2926, 2876, 1497, 1456, 1399, 1266, 1225, 1096, 1075, 1022, 750, 698 $cm^{-1}$; $^1H$ NMR (100 MHz) $\delta$ = 4.04 (s, 4 H), 7.2—7.4 (m, 10 H); $^{19}F$ NMR (94 MHz) $\delta$ = −59.71 (s); $^{13}C$ NMR (75.5 MHz) $\delta$ = 49.5 (q, *J* = 2 Hz), 125.1 (d, $^1J_{C-F}$ = 256 Hz), 127.5 (s), 128.4 (s), 128.6 (s), 136.5 (s); MS *m/z* (rel intensity) 265 ($M^+$; 2), 174 (18), 152 (6), 149 (6), 93 (7), 92 (59), 91 (100), 77 (11), 69 (13), 65 (22). Found: *m/z* 265.1066. Calcd for $C_{15}H_{14}F_3N$: M, 265.1078.

**Benzyl(propyl)(trifluoromethyl)amine (3s).** This compound was similarly prepared in 84% yield as a colorless oil, bp 95—100 °C/0.8 mmHg. IR 3034, 2973, 2938, 2880, 1497, 1456, 1401, 1231, 1156, 1071, 1007, 735, 698 $cm^{-1}$; $^1H$ NMR (100 MHz) $\delta$ = 0.79 (t, *J* = 6 Hz, 3 H), 1.46 (sextet, *J* = 6 Hz, 2 H), 2.80 (qt, *J* = 1, 6 Hz, 2 H), 4.05 (s, 2 H), 7.3—7.4 (m, 5 H); $^{19}F$ NMR (94 MHz) $\delta$ = −60.90 (s); $^{13}C$ NMR (75.5 MHz) $\delta$ = 11.2 (s), 20.8 (s), 48.6 (s), 50.5 (q, *J* = 2 Hz), 125.3 (q, $^1J_{C-F}$ = 254 Hz), 127.4 (s), 128.0 (s), 128.4 (s), 137.5 (s); MS *m/z* (rel intensity) 217 ($M^+$; 2), 188 (5), 155 (2), 126 (8), 96 (4), 92 (10), 91 (100), 69 (17), 65 (29). Found: *m/z* 217.1080. Calcd for $C_{11}H_{14}F_3N$: M, 217.1078.

**A General Procedure for the Preparation of Bromoaryl(trifluoromethyl)amines:** To a stirred suspension of $TBAH_2F_3$ (10 mmol) and DBH (10 mmol) in dichloromethane (4.0 mL) was added dropwise a solution of a dithiocarbamate (2.0 mmol) in dichloromethane (1.0 mL) at room temperature, and the reaction mixture was heated to reflux until all of the substrate was consumed. The resulting mixture was treated with an aq $NaHSO_3$/$NaHCO_3$/NaOH (pH 10) solution at 0 °C. The pH value of the mixture was adjusted at 10 with NaOH, and the organic phase was separated. The aq phase was extracted with diethyl ether three times. The combined organic phase was dried over sodium sulfate, filtered through a pad of Celite/silica gel (Wako Gel C-100), and concentrated. The residue was purified by column chromatography or bulb-to-bulb distillation to give the desired trifluoromethylamines. The yields and spectra of the products were as follows.

***N*-Methyl-*N*-trifluoromethyl-4-bromoaniline (4m).** Yield: 96%. A colorless oil, bp 120 °C/10 mmHg; $R_f$ = 0.70 (hexane : $Et_2O$ = 10 : 1). IR 2984, 2920, 1495, 1437, 1281, 1262, 1198, 1148, 1090, 1059, 1013, 831 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta$ = 3.01 (q, *J* = 1 Hz, 3 H), 7.10—7.25 (m, 2 H), 7.43—7.49 (m, 2 H); $^{19}F$ NMR (188 MHz) $\delta$ = −61.12 (s); $^{13}C$ NMR (50.3 MHz) $\delta$ = 36.1 (q, *J* = 2 Hz), 119.6 (s), 123.2 (q, $^1J_{C-F}$ = 256 Hz), 126.4 (q, *J* = 2 Hz), 132.2 (s), 141.8 (s); MS *m/z* (rel intensity) 256 ($M^+$+3; 6), 255 ($M^+$+2; 63), 254 ($M^+$+1; 23), 253 ($M^+$; 65), 236 (8), 234 (8), 186 (10), 185 (10), 184 (17), 183 (8), 182 (6), 174 (9), 173 (15), 159 (37), 157 (17), 155 (19), 105 (48), 104 (30), 90 (28), 77 (67), 78 (33), 76 (44), 69 (100), 63 (50). Found: C, 37.82; H, 2.57; N, 5.22%. Calcd for $C_8H_7BrF_3N$: C, 37.82; H, 2.78; N, 5.51%.

***N*-Ethyl-*N*-trifluoromethyl-4-bromoaniline (4n).** Yield: 83%. A colorless oil, bp 116 °C/0.6 mmHg; $R_f$ = 0.65 (hexane). IR 2984, 2941, 1493, 1472, 1337, 1269, 1194, 1144, 1100, 1012, 908, 831 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta$ = 1.08 (dt, *J* = 1, 7 Hz, 3 H), 3.40 (dq, *J* = 1, 7 Hz, 3 H), 7.12 (d, *J* = 9 Hz, 2 H), 7.48 (d, *J* = 9 Hz, 2 H); $^{19}F$ NMR (188 MHz) $\delta$ = −58.39 (s); $^{13}C$ NMR (50.3 MHz) $\delta$ = 13.6 (s), 43.8 (q, *J* = 2 Hz), 120.2 (s), 123.2 (q, $^1J_{C-F}$ = 256 Hz), 128.2 (q, *J* = 2 Hz), 132.3 (s), 139.8 (s); MS *m/z* (rel intensity)

288 ($M^+$+3; 9), 287 ($M^+$+2; 71), 286 ($M^+$+1; 12), 285 ($M^+$; 68), 273 (18), 272 (58), 271 (21), 270 (100), 259 (15), 257 (17), 240 (14), 239 (38), 238 (16), 237 (35), 203 (42), 202 (23), 201 (44), 200 (20), 192 (28), 177 (24), 158 (17), 113 (23), 108 (26), 94 (44), 81 (18), 75 (17), 69 (47). Found: C, 40.42; H, 3.32; N, 5.19%. Calcd for $C_9H_9BrF_3N$: C, 40.32; H, 3.38; N, 5.22%.

***N*-Propyl-*N*-trifluoromethyl-4-bromoaniline (4o).** Yield: 68%. A colorless oil, bp 110 °C/1.5 mmHg; $R_f$ = 0.62 (hexane). IR 2973, 2938, 2880, 1493, 1458, 1339, 1240, 1194, 1146, 1063, 1013, 930, 833, 795, 723 $cm^{-1}$; $^1$H NMR (90 MHz) $\delta$ = 0.88 (t, $J$ = 7 Hz, 3 H), 1.13—1.91 (m, 2 H), 3.27 (t, $J$ = 7 Hz, 2 H), 7.12 (d, $J$ = 9 Hz, 2 H), 7.47 (d, $J$ = 9 Hz, 2 H); $^{19}$F NMR (188 MHz) $\delta$ = −58.57 (s); $^{13}$C NMR (50.3 MHz) $\delta$ = 10.9 (s), 21.3 (s), 50.7 (q, $J$ = 1 Hz), 120.3 (s), 123.2 (q, $^1J_{C-F}$ = 255 Hz), 128.5 (q, $J$ = 2 Hz), 132.3 (s), 140.1 (s); MS *m/z* (rel intensity) 284 ($M^+$+3; 8), 283 ($M^+$+2; 63), 282 ($M^+$+1; 9), 281 ($M^+$; 64), 255 (21), 254 (97), 253 (24), 252 (100), 239 (11), 221 (15), 220 (15), 219 (13), 185 (34), 184 (19), 183 (31), 182 (17), 173 (74), 159 (19), 157 (39), 155 (36), 95 (19), 90 (14), 78 (48), 76 (58), 75 (54), 69 (40). Found: C, 42.49; H, 3.83; N, 4.89%. Calcd for $C_{10}H_{11}BrF_3N$: C, 42.58; H, 3.93; N, 4.97%.

***N*-Hexyl-*N*-trifluoromethyl-4-bromoaniline (4p).** Yield: 71% (in boiling $CH_2Cl_2$), 86% (0 °C). A colorless oil, bp 132 °C/0.68 mmHg; $R_f$ = 0.73 (hexane). IR 2959, 2932, 2861, 1493, 1375, 1258, 1194, 1100, 1071, 1061, 1013, 920, 831 $cm^{-1}$; $^1$H NMR (200 MHz) $\delta$ = 0.86 (t, $J$ = 7 Hz, 3 H), 1.02—1.57 (m, 8 H), 3.27 (t, $J$ = 7 Hz, 3 H), 7.11 (d, $J$ = 9 Hz, 2 H), 7.52 (d, $J$ = 9 Hz, 2 H); $^{19}$F NMR (188 MHz) $\delta$ = −58.57 (s); $^{13}$C NMR (50.3 MHz) $\delta$ = 13.9 (s), 22.5 (s), 26.2 (s), 28.0 (s), 31.3 (s), 49.0 (q, $J$ = 1 Hz), 120.3 (s), 123.2 (q, $^1J_{C-F}$ = 255 Hz), 128.5 (q, $J$ = 2 Hz), 132.3 (s), 140.1 (s); MS *m/z* (rel intensity) 326 ($M^+$+3; 8), 325 ($M^+$+2; 47), 324 ($M^+$+1; 8), 323 ($M^+$; 50), 301 (13), 255 (26), 254 (100), 252 (97), 241 (48), 240 (49), 232 (18), 230 (20), 219 (19), 217 (13), 186 (15), 185 (27), 184 (24), 183 (27), 182 (14), 174 (13), 173 (54), 159 (24), 157 (26), 155 (29), 95 (11), 90 (11), 78 (25), 77 (17), 76 (39), 75 (29), 69 (23). Found: C, 48.44; H, 5.15; N, 4.46%. Calcd for $C_{13}H_{17}BrF_3N$: C, 48.16; H, 5.29; N, 4.32%.

***N*-Octyl-*N*-trifluoromethyl-4-bromoaniline (4q).** Yield: 79% (0 °C). An alternative procedure follows. A polypropylene round-bottom tube was charged with NBS (0.45 g, 2.5 mmol), 70 wt% HF/pyridine (0.26 mL), and dichloromethane (1.0 mL). To this suspension was added a solution of **2s** (0.16 g, 0.50 mmol) in dichloromethane (1.0 mL) at 0 °C, and the whole mixture was stirred for 30 min at 0 °C before quenching with an aq $NaHSO_3$/$NaHCO_3$/NaOH (pH 10) solution at 0 °C. The organic phase was separated; the aqueous phase was extracted with diethyl ether three times. The combined organic phase was dried over sodium sulfate, filtrated (Wako Gel C-100), and concentrated. The residue was purified by column chromatography (pentane) to give **4q** (0.10 g, 0.30 mmol) in 60% yield along with the starting material **2q** (0.05 g, 0.16 mmol, 33%).

**4q:** A colorless oil, bp 183 °C/0.58 mmHg; $R_f$ = 0.71 (hexane). IR 2957, 2930, 2860, 1493, 1375, 1273, 1260, 1192, 1073, 1051, 1013, 908, 831 $cm^{-1}$; $^1$H NMR (200 MHz) $\delta$ = 0.87 (t, $J$ = 6 Hz, 3 H), 0.91—1.37 (m, 12 H), 3.29 (t, $J$ = 6 Hz, 2 H), 7.12 (d, $J$ = 9 Hz, 2 H), 7.48 (d, $J$ = 9 Hz, 2 H); $^{19}$F NMR (188 MHz) $\delta$ = −58.59 (s); $^{13}$C NMR (50.3 MHz) $\delta$ = 14.0 (s), 22.6 (s), 26.6 (s), 28.1 (s), 29.1 (s), 29.2 (s), 31.8 (s), 49.0 (q, $J$ = 1 Hz), 120.3 (s), 123.3 (q, $^1J_{C-F}$ = 255 Hz), 128.5 (q, $J$ = 2 Hz), 132.3 (s), 140.1 (s); MS *m/z* (rel intensity) 354 ($M^+$+3; 11), 353 ($M^+$+2; 55), 352 ($M^+$+1; 11), 351 ($M^+$; 56), 255 (27), 254 (100), 253 (31), 252 (99), 241 (55), 239 (60), 186 (11), 185 (22), 184 (11), 183 (19), 174 (16), 173 (55), 159 (14), 157 (22), 155 (20), 78 (19), 77 (12), 76 (22), 75 (18), 71 (33), 69 (31). Found: *m/z* 351.0803. Calcd for $C_{15}H_{21}BrF_3N$: M, 351.0809.

**A General Procedure for the Preparation of (Trifluoromethylamino)pyridines (7) and -pyrimidines (11).** To a stirred suspension of $TBAH_2F_3$ (25 mmol) and DBH (20 mmol) in dichloromethane (10 mL) was added dropwise a solution of a dithiocarbamate (5.0 mmol) in dichloromethane (5.0 mL) at 0 °C. The reaction mixture was stirred at 0 °C until all of the substrate was consumed, and was poured into an aq buffer solution of $NaHCO_3$/NaOH/$NaHSO_3$ (pH 10). The resultant was extracted with diethyl ether three times. The combined organic layer was dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography or bulb-to-bulb distillation to give the corresponding trifluoromethylamines. The yields and spectroscopic properties of the products are given below.

**Methyl(2-pyridyl)(trifluoromethyl)amine (7a).** Yield: 72%. A colorless oil; $R_f$ = 0.68 (hexane : $Et_2O$ = 10 : 1). IR 3018, 2958, 2928, 1595, 1577, 1482, 1426, 1351, 1339, 1276, 1200, 1141, 1100, 1074, 778, 741, 663 $cm^{-1}$; $^1$H NMR (200 MHz) $\delta$ = 3.26 (q, $J$ = 2 Hz, 3 H), 6.97 (ddd, $J$ = 1, 4, 6 Hz, 1 H), 7.06—7.13 (dm, $J$ = 8 Hz, 1 H), 7.61 (ddd, $J$ = 2, 7, 9 Hz, 1 H), 8.35 (ddd, $J$ = 1, 2, 5 Hz, 1 H); $^{19}$F NMR (188 MHz) $\delta$ = −57.9 (dq, $J$ = 2 Hz); $^{13}$C NMR (50.3 MHz) $\delta$ = 32.1 (s), 113.6 (s), 118.3 (s), 122.9 (q, $^1J_{C-F}$ = 256 Hz), 137.5 (s), 147.9 (s), 153.8 (s); MS *m/z* (rel intensity) 176 ($M^+$; 28), 157 (7), 107 (56), 84 (100), 80 (15), 79 (69), 78 (55). Found: *m/z* 176.0587. Calcd for $C_7H_7F_3N_2$: M, 176.0561.

**Ethyl(2-pyridyl)(trifluoromethyl)amine (7b).** Yield: 75%. A colorless oil; $R_f$ = 0.50 (hexane : $Et_2O$ = 10 : 1). IR 2980, 2940, 1595, 1482, 1437, 1331, 1260, 1196, 1140, 1102, 941, 776 $cm^{-1}$; $^1$H NMR (300 MHz) $\delta$ = 1.34 (t, $J$ = 7 Hz, 3 H), 4.00 (qq, $J$ = 2, 7 Hz, 2 H), 7.07 (ddd, $J$ = 1, 5, 7 Hz, 1 H), 7.17 (ddd, $J$ = 1, 1, 10 Hz, 1 H), 7.72 (ddd, $J$ = 2, 7, 10 Hz, 1 H), 8.50 (ddd, $J$ = 1, 2, 5 Hz, 1 H); $^{19}$F NMR (188 MHz) $\delta$ = −55.9 (s); $^{13}$C NMR (75.5 MHz) $\delta$ = 14.2 (s), 40.4 (s), 113.5 (q, $J$ = 4 Hz), 118.0 (s), 123.0 (q, $^1J_{C-F}$ = 258 Hz), 137.6 (s), 148.0 (s), 152.9 (s); MS *m/z* (rel intensity) 191 ($M^+$+1; 2), 190 ($M^+$; 13), 176 (3), 175 (36), 155 (11), 142 (24), 121 (34), 80 (8), 79 (85), 78 (100), 69 (21). Found: *m/z* 190.0716. Calcd for $C_8H_9F_3N_2$: M, 190.0718.

**Hexyl(2-pyridyl)(trifluoromethyl)amine (7c).** Yield: 67%. A colorless oil; $R_f$ = 0.68 (hexane : $Et_2O$ = 5 : 1). IR 2959, 2933, 2861, 1593, 1481, 1437, 1388, 1334, 1257, 1194, 1145, 1099, 776 $cm^{-1}$; $^1$H NMR (200 MHz) $\delta$ = 0.87 (t, $J$ = 6 Hz, 3 H), 1.26—1.43 (m, 6 H), 1.53—1.63 (m, 2 H), 3.72—3.83 (m, 2 H), 6.94 (ddd, $J$ = 1, 5, 7 Hz, 1 H), 7.05 (dm, $J$ = 9 Hz, 1 H), 7.59 (ddd, $J$ = 2, 7, 9 Hz, 1 H), 8.34 (ddd, $J$ = 1, 2, 5 Hz, 1 H); $^{19}$F NMR (188 MHz) $\delta$ = −55.9 (dt, $J$ = 2, 2 Hz); $^{13}$C NMR (50.3 MHz) $\delta$ = 13.8 (s), 22.5 (s), 26.3 (s), 28.7 (s), 31.4 (s), 45.3 (s), 113.6 (s), 118.0 (s), 123.0 (q, $^1J_{C-F}$ = 256 Hz), 137.4 (s), 147.9 (s), 153.1 (s); MS *m/z* (rel intensity) 246 ($M^+$; 12), 206 (6), 189 (17), 177 (24), 175 (72), 169 (31), 162 (74), 156 (5), 142 (100), 107 (24), 78 (97). Found: *m/z* 246.1354. Calcd for $C_{12}H_{17}F_3N_2$: M, 246.1344.

**Octyl(2-pyridyl)(trifluoromethyl)amine (7d).** Yield: 76% as performed at −20 °C. A colorless oil; $R_f$ = 0.77 (hexane : $Et_2O$ = 5 : 1). IR 2958, 2932, 1730, 1607, 1573, 1497, 1436, 1393, 1357, 1330, 1297, 1276, 1199, 1126, 1072, 1020, 782, 617 $cm^{-1}$; $^1$H NMR (200 MHz) $\delta$ = 0.87 (t, $J$ = 6 Hz, 3 H), 1.17—1.43 (m, 10 H), 1.53—1.66 (m, 2 H), 3.72—3.83 (m, 2 H), 6.94 (ddd, $J$ = 1, 5, 7 Hz, 1 H), 7.05 (dm, $J$ = 9 Hz, 1 H), 7.59 (ddd, $J$ = 2, 7, 9 Hz, 1 H), 8.34 (ddd, $J$ = 1, 2, 5 Hz, 1 H); $^{19}$F NMR (188 MHz) $\delta$ = −55.8 (dt, $J$ = 2, 2 Hz); $^{13}$C NMR (50.3 MHz) $\delta$ = 14.0 (s), 22.6 (s), 26.7

(s), 28.8 (s), 29.2 (s), 31.8 (s), 45.3 (s), 113.7 (s), 118.0 (s), 123.0 (q, $^1J_{C-F}$ = 257 Hz), 137.5 (s), 148.0 (s), 153.1 (s); MS *m/z* (rel intensity) 274 ($M^+$; 10), 205 (12), 189 (13), 175 (53), 162 (93), 143 (22), 142 (80), 107 (18), 106 (16), 79 (41), 78 (100). Found: *m/z* 274.1663. Calcd for $C_{14}H_{21}F_3N_2$: M, 274.1657.

**Dodecyl(2-pyridyl)(trifluoromethyl)amine (7e).** Yield: 86% (prepared at −20 °C). A colorless oil; $R_f$ = 0.66 (hexane : $Et_2O$ = 10 : 1). IR 2927, 2856, 1594, 1575, 1481, 1468, 1437, 1387, 1334, 1264, 1194, 1163, 1138, 1100, 1078, 755, 738 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta$ = 0.87 (t, *J* = 6 Hz, 3 H), 1.15—1.37 (m, 18 H), 1.53—1.67 (m, 2 H), 3.72—3.82 (m, 2 H), 6.94 (ddd, *J* = 1, 5, 7 Hz, 1 H), 7.05 (dm, *J* = 9 Hz, 1 H), 7.59 (ddd, *J* = 2, 7, 9 Hz, 1 H), 8.34 (ddd, *J* = 1, 2, 5 Hz, 1 H); $^{19}F$ NMR (188 MHz) $\delta$ = −55.8 (dt, *J* = 2, 2 Hz); $^{13}C$ NMR (50.3 MHz) $\delta$ = 14.0 (s), 22.7 (s), 26.7 (s), 28.8 (s), 29.3 (s), 29.5 (s), 29.6 (s), 31.9 (s), 45.3 (s), 113.7 (s), 118.0 (s), 122.9 (q, $^1J_{C-F}$ = 257 Hz), 137.4 (s), 148.0 (s), 153.1 (s); MS *m/z* (rel intensity) 330 ($M^+$; 5), 261 (8), 232 (11), 204 (7), 189 (16), 176 (12), 175 (52), 169 (22), 163 (10), 162 (100), 142 (76), 106 (21), 78 (83). Found: *m/z* 330.2285. Calcd for $C_{18}H_{29}F_3N_2$: M, 330.2283.

**Benzyl(2-pyridyl)(trifluoromethyl)amine (7f).** Yield: 80%. A colorless oil; $R_f$ = 0.42 (hexane : $Et_2O$ = 10 : 1). IR 3067, 3034, 1591, 1479, 1436, 1382, 1332, 1270, 1232, 1105, 775, 698 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta$ = 5.05 (q, *J* = 2 Hz, 2 H), 6.95 (ddd, *J* = 1, 5, 7 Hz, 1 H), 7.07 (dm, *J* = 8 Hz, 1 H), 7.21—7.33 (m, 5 H), 7.59 (ddd, *J* = 2, 7, 9 Hz, 1 H), 8.33 (ddd, *J* = 1, 2, 5 Hz, 1 H); $^{19}F$ NMR (188 MHz) $\delta$ = −55.6 (dq, *J* = 2, 2 Hz); $^{13}C$ NMR (50.3 MHz) $\delta$ = 48.5 (s), 113.35 (s), 113.43 (s), 118.4 (s), 123.0 (q, $^1J_{C-F}$ = 258 Hz), 127.2 (s), 128.5 (s), 137.8 (s), 138.2 (s), 148.1 (s), 153.0 (s); MS *m/z* (rel intensity) 253 ($M^+$+1; 10), 252 ($M^+$; 71), 184 (11), 174 (9), 91 (100), 79 (52), 78 (35). Found: *m/z* 252.0867. Calcd for $C_{13}H_{11}F_3N_2$: M, 252.0874.

**Methyl(2-pyrimidinyl)(trifluoromethyl)amine (11a).** Yield: 38%. A colorless oil; $R_f$ = 0.57 (hexane : $Et_2O$ = 1 : 1). IR 2970, 2950, 1588, 1568, 1470, 1409, 1372, 1326, 1266, 1210, 1135, 1071, 989, 926, 806, 679, 618 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta$ = 3.36 (q, *J* = 2 Hz, 3 H), 6.89 (t, *J* = 5 Hz, 1 H), 8.52 (d, *J* = 5 Hz, 2 H); $^{19}F$ NMR (188 MHz) $\delta$ = −57.1 (q, *J* = 2 Hz); $^{13}C$ NMR (50.3 MHz) $\delta$ = 31.5 (s), 114.6 (s), 122.0 (q, $^1J_{C-F}$ = 258 Hz), 157.6 (s), 159.3 (s); MS *m/z* (rel intensity) 177 ($M^+$; 45), 158 (11), 108 (54), 84 (75), 80 (100), 79 (34), 78 (6). Found: *m/z* 177.0509. Calcd for $C_6H_6F_3N_3$: M, 177.0514.

**Propyl(2-pyrimidinyl)(trifluoromethyl)amine (11b).** Yield: 50%. A colorless oil; $R_f$ = 0.22 (hexane : $Et_2O$ = 10 : 1). IR 2971, 2882, 1588, 1564, 1470, 1429, 1389, 1331, 1304, 1267, 1235, 1140, 1107, 1073, 955, 806 $cm^{-1}$; $^1H$ NMR (300 MHz) $\delta$ = 1.05 (t, *J* = 8 Hz, 3 H), 1.81 (sextet, *J* = 8 Hz, 2 H), 3.95 (qt, *J* = 2, 8 Hz, 2 H), 6.99 (t, *J* = 5 Hz, 1 H), 8.63 (d, *J* = 5 Hz, 2 H); $^{19}F$ NMR (188 MHz) $\delta$ = −57.9 (t, *J* = 2 Hz); $^{13}C$ NMR (75.5 MHz) $\delta$ = 11.0 (s), 22.0 (s), 46.6 (s), 114.4 (s), 122.1 (q, $^1J_{C-F}$ = 259 Hz), 157.6 (s), 158.9 (s); MS *m/z* (rel intensity) 206 ($M^+$+1; 4), 205 ($M^+$; 32), 176 (44), 163 (16), 144 (15), 143 (33), 80 (45), 79 (100), 78 (44), 69 (14). Found: *m/z* 205.0823. Calcd for $C_8H_{10}F_3N_3$: M, 205.0827.

**Hexyl(2-pyrimidinyl)(trifluoromethyl)amine (11c).** Yield: 58%. A colorless oil; $R_f$ = 0.51 (hexane : $Et_2O$ = 5 : 1). IR 2960, 2933, 2861, 1588, 1565, 1470, 1429, 1391, 1333, 1250, 1194, 1143, 1104, 1072, 805, 637 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta$ = 0.88 (t, *J* = 7 Hz, 3 H), 1.30—1.36 (m, 6 H), 1.58—1.69 (m, 2 H), 3.80—3.91 (m, 2 H), 6.87 (t, *J* = 5 Hz, 1 H), 8.51 (d, *J* = 5 Hz, 2 H); $^{19}F$ NMR (188 MHz) $\delta$ = −55.8 (t, *J* = 2 Hz); $^{13}C$ NMR (50.3 MHz) $\delta$ = 13.9 (s), 22.5 (s), 26.2 (s), 28.7 (s), 31.4 (s), 45.1 (s), 114.4 (s), 122.1 (q, $^1J_{C-F}$ = 259 Hz), 157.6 (s), 159.0 (s); MS *m/z* (rel intensity) 248 ($M^+$+1; 7), 247 ($M^+$; 55), 205 (17), 190 (11), 177 (16), 176 (100), 163 (28), 144 (57), 143 (45), 80 (39), 79 (77). Found: *m/z* 247.1284. Calcd for $C_{11}H_{16}F_3N_3$: M, 247.1296.

**Octyl(2-pyrimidinyl)(trifluoromethyl)amine (11d).** Yield: 80%. A colorless oil; $R_f$ = 0.44 (hexane : $Et_2O$ = 5 : 1). IR 2958, 2929, 2858, 1588, 1564, 1470, 1429, 1391, 1383, 1333, 1255, 1235, 1206, 1177, 1141, 1104, 1072, 805, 637 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta$ = 0.87 (t, *J* = 7 Hz, 3 H), 1.26—1.30 (m, 10 H), 1.57—1.66 (m, 2 H), 3.80—3.91 (m, 2 H), 6.87 (t, *J* = 5 Hz, 1 H), 8.51 (d, *J* = 5 Hz, 2 H); $^{19}F$ NMR (188 MHz) $\delta$ = −55.8 (t, *J* = 2 Hz); $^{13}C$ NMR (50.3 MHz) $\delta$ = 14.0 (s), 22.6 (s), 26.6 (s), 28.7 (s), 29.2 (s), 31.7 (s), 45.0 (s), 114.4 (s), 122.1 (q, $^1J_{C-F}$ = 259 Hz), 157.6 (s), 159.0 (s); MS *m/z* (rel intensity) 276 ($M^+$+1; 10), 275 ($M^+$; 62), 205 (22), 191 (14), 190 (12), 177 (20), 176 (100), 163 (31), 144 (73), 143 (50), 108 (13), 80 (44), 79 (86). Found: *m/z* 275.1615. Calcd for $C_{13}H_{20}F_3N_3$: M, 275.1609.

**Dodecyl(2-pyrimidinyl)(trifluoromethyl)amine (11e).** Yield: 63%. A colorless oil; $R_f$ = 0.38 (hexane : $Et_2O$ = 5 : 1). IR 2930, 2917, 2850, 1586, 1571, 1470, 1430, 1392, 1382, 1340, 1253, 1151, 1130, 1102, 854, 638 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta$ = 0.87 (t, *J* = 6 Hz, 3 H), 1.26—1.31 (m, 18 H), 1.57—1.69 (m, 2 H), 3.80—3.91 (m, 2 H), 6.86 (t, *J* = 5 Hz, 1 H), 8.50 (d, *J* = 5 Hz, 2 H); $^{19}F$ NMR (188 MHz) $\delta$ = −55.8 (t, *J* = 2 Hz); $^{13}C$ NMR (50.3 MHz) $\delta$ = 14.0 (s), 22.6 (s), 26.6 (s), 28.7 (s), 29.2 (s), 29.3 (s), 29.6 (s), 31.9 (s), 45.0 (s), 114.4 (s), 122.2 (q, $^1J_{C-F}$ = 259 Hz), 157.6 (s), 159.0 (s); MS *m/z* (rel intensity) 332 ($M^+$+1; 20), 331 ($M^+$; 100), 205 (18), 191 (11), 190 (10), 176 (79), 164 (20), 144 (63), 143 (30), 78 (49). Found: *m/z* 331.2248. Calcd for $C_{17}H_{28}F_3N_3$: M, 331.2235.

Preparation of 5-bromo-2-(trifluoromethylamino)pyridines **8** and -pyrimidines **12** was carried out in a procedure similar to that for **4**. Yields and spectroscopic properties are as follows.

**5- Bromo- 2- [methyl(trifluoromethyl)amino]pyridine (8a).** Yield: 78%. A colorless oil; $R_f$ = 0.56 (hexane : $Et_2O$ = 5 : 1). IR 2992, 2956, 2935, 2899, 1583, 1563, 1526, 1478, 1434, 1384, 1355, 1324, 1273, 1244, 1199, 1121, 1108, 1071, 1002, 916, 821, 616 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta$ = 3.24 (q, *J* = 2 Hz, 3 H), 7.00 (dd, *J* = 2, 8 Hz, 1 H), 7.70 (dd, *J* = 2, 8 Hz, 1 H), 8.38 (d, *J* = 2 Hz, 1 H); $^{19}F$ NMR (188 MHz) $\delta$ = −57.9 (dq, *J* = 2, 2 Hz); $^{13}C$ NMR (50.3 MHz) $\delta$ = 32.0 (s), 113.7 (s), 114.7 (s), 122.6 (q, $^1J_{C-F}$ = 257 Hz), 139.9 (s), 148.6 (s), 152.3 (s); MS *m/z* (rel intensity) 257 ($M^+$+3; 5), 256 ($M^+$+2; 28), 255 ($M^+$+1; 9), 254 ($M^+$; 35), 187 (68), 185 (70), 160 (52), 159 (51), 158 (100), 157 (63), 156 (40), 106 (12), 78 (92). Found: *m/z* 253.9678. Calcd for $C_7H_6BrF_3N_2$: M, 253.9667.

**5-Bromo-2-[ethyl(trifluoromethyl)amino]pyridine (8b).** Yield: 82%. A colorless oil, bp 80 °C/2 mmHg; $R_f$ = 0.48 (hexane : $Et_2O$ = 20 : 1). IR 2986, 2940, 2860, 1584, 1559, 1480, 1381, 1320, 1260, 1244, 1194, 1132, 1105, 1067, 943, 819 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta$ = 1.21 (dt, *J* = 0.4, 7 Hz, 3 H), 3.86 (qq, *J* = 2, 7 Hz, 2 H), 6.96 (dqd, *J* = 1, 2, 9 Hz, 1 H), 7.68 (dd, *J* = 3, 9 Hz, 1 H), 8.38 (dd, *J* = 1, 3 Hz, 1 H); $^{19}F$ NMR (188 MHz) $\delta$ = −56.10 (dm, *J* = 2 Hz); $^{13}C$ NMR (50.3 MHz) $\delta$ = 14.0 (s), 40.4 (s), 113.3 (s), 114.4 (m), 122.7 (q, *J* = 258 Hz), 140.0 (s), 148.8 (s), 151.5 (s); MS *m/z* (rel intensity) 271 ($M^+$+3; 4), 270 ($M^+$+2; 38), 269 ($M^+$+1; 6), 268 ($M^+$; 40), 256 (11), 255 (97), 254 (12), 253 (100), 235 (42), 233 (42), 223 (15), 222 (60), 220 (67), 201 (77), 199 (76), 159 (94), 158 (92), 157 (98), 156 (98), 119 (39), 92 (28), 78 (86), 77 (63), 76 (84), 69 (90). Found: C, 35.89; H, 3.09; N, 10.52%. Calcd for $C_8H_8BrF_3N_2$: C, 35.71; H, 3.00; N, 10.41%.

**5-Bromo-2-[hexyl(trifluoromethyl)amino]pyridine (8c).** Yield: 89%. A colorless oil; $R_f$ = 0.75 (hexane : $Et_2O$ = 20 : 1). IR 2959, 2933, 2860, 1583, 1560, 1477, 1381, 1300, 1255, 1192, 1142, 1105, 1070, 1001, 819 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta$ = 0.87 (t, *J* = 7 Hz, 3 H), 1.22—1.34 (m, 6 H), 1.43—1.62 (m, 2 H), 3.70—3.80 (m,

2 H), 6.94 (dm, $J$ = 9 Hz, 1 H), 7.67 (dd, $J$ = 3, 9 Hz, 1 H), 8.36 (dd, $J$ = 1, 3 Hz, 1 H); $^{19}$F NMR (188 MHz) $\delta$ = −56.0 (dt, $J$ = 2, 2 Hz); $^{13}$C NMR (50.3 MHz) $\delta$ = 13.9 (s), 22.5 (s), 26.3 (s), 28.6 (s), 31.4 (s), 45.4 (s), 113.3 (s), 114.5 (s), 122.7 (q, $^{1}J_{C-F}$ = 257 Hz), 139.9 (s), 148.7 (s), 151.7 (s); MS *m/z* (rel intensity) 326 ($M^+$+2; 15), 324 ($M^+$; 15), 255 (87), 253 (75), 242 (56), 240 (59), 222 (100), 220 (92), 187 (10), 186 (14), 185 (15), 184 (12), 158 (47), 156 (42), 77 (7). Found: *m/z* 324.0451. Calcd for $C_{12}H_{16}BrF_3N_2$: M, 324.0449.

**5-Bromo-2-[octyl(trifluoromethyl)amino]pyridine (8d).** Yield: 89%. A colorless oil; $R_f$ = 0.68 (hexane : $Et_2O$ = 20 : 1). IR 2958, 2929, 2857, 1583, 1560, 1477, 1379, 1320, 1302, 1266, 1244, 1192, 1141, 1106, 819 cm$^{-1}$; $^1$H NMR (200 MHz) $\delta$ = 0.87 (t, $J$ = 7 Hz, 3 H), 1.18—1.26 (m, 10 H), 1.53—1.62 (m, 2 H), 3.73—3.80 (m, 2 H), 6.95 (dm, $J$ = 9 Hz, 1 H), 7.67 (dd, $J$ = 3, 9 Hz, 1 H), 8.36 (dd, $J$ = 1, 3 Hz, 1 H); $^{19}$F NMR (188 MHz) $\delta$ = −56.1 (dt, $J$ = 2, 2 Hz); $^{13}$C NMR (50.3 MHz) $\delta$ = 14.0 (s), 22.6 (s), 26.6 (s), 28.6 (s), 29.1 (s), 31.8 (s), 45.3 (s), 113.3 (s), 114.6 (s), 122.7 (q, $^{1}J_{C-F}$ = 257 Hz), 140.0 (s), 148.7 (s), 151.7 (s); MS *m/z* (rel intensity) 354 ($M^+$+2; 5), 352 ($M^+$; 5), 291 (7), 289 (6), 255 (60), 253 (57), 242 (63), 240 (62), 222 (96), 220 (100), 158 (81), 156 (68), 77 (23). Found: *m/z* 352.0754. Calcd for $C_{14}H_{20}BrF_3N_2$: M, 352.0762.

**5- Bromo- 2- [dodecyl(trifluoromethyl)amino]pyridine (8e).** Yield: 90%. A colorless oil; $R_f$ = 0.81 (hexane : $Et_2O$ = 20 : 1). IR 2956, 2926, 2855, 1583, 1477, 1380, 1320, 1305, 1264, 1244, 1193, 1157, 1138, 1107, 1071, 1000, 819 cm$^{-1}$; $^1$H NMR (200 MHz) $\delta$ = 0.87 (t, $J$ = 7 Hz, 3 H), 1.17—1.34 (m, 18 H), 1.53—1.62 (m, 2 H), 3.70—3.80 (m, 2 H), 6.95 (dm, $J$ = 9 Hz, 1 H), 7.67 (dd, $J$ = 3, 9 Hz, 1 H), 8.36 (dd, $J$ = 1, 3 Hz, 1 H); $^{19}$F NMR (188 MHz) $\delta$ = −56.1 (dt, $J$ = 2, 2 Hz); $^{13}$C NMR (50.3 MHz) $\delta$ = 14.1 (s), 22.7 (s), 26.6 (s), 28.6 (s), 29.2 (s), 29.3 (s), 29.5 (s), 29.6 (s), 31.9 (s), 45.4 (s), 113.3 (s), 114.5 (s), 122.7 (q, $^{1}J_{C-F}$ = 257 Hz), 139.9 (s), 148.7 (s), 151.7 (s); MS *m/z* (rel intensity) 410 ($M^+$+2; 5), 408 ($M^+$; 5), 341 (4), 339 (4), 312 (12), 310 (13), 298 (6), 296 (7), 284 (7), 282 (7), 242 (90), 240 (95), 222 (100), 220 (93), 200 (7), 198 (9), 186 (29), 184 (30), 158 (75), 156 (61), 77 (23). Found: *m/z* 408.1386. Calcd for $C_{18}H_{28}BrF_3N_2$: M, 408.1388.

**5- Bromo- 2- [benzyl(trifluoromethyl)amino]pyridine (8f).** Yield: 78%. A colorless oil; $R_f$ = 0.78 (hexane : $Et_2O$ = 10 : 1). IR 3067, 3034, 2961, 1582, 1563, 1512, 1496, 1476, 1455, 1437, 1379, 1320, 1270, 1244, 1232, 1192, 1110, 1065, 1010, 1002, 820, 699 cm$^{-1}$; $^1$H NMR (200 MHz) $\delta$ = 5.01 (q, $J$ = 2 Hz, 2 H), 6.97 (dm, $J$ = 8 Hz, 1 H), 7.25—7.31 (m, 5 H), 7.68 (dd, $J$ = 3, 9 Hz, 1 H), 8.35 (dd, $J$ = 1, 3 Hz, 1 H); $^{19}$F NMR (188 MHz) $\delta$ = −55.8 (dt, $J$ = 2, 2 Hz); $^{13}$C NMR (50.3 MHz) $\delta$ = 48.4 (s), 113.8 (s), 114.4 (s), 122.7 (q, $^{1}J_{C-F}$ = 258 Hz), 127.1 (s), 127.3 (s), 128.5 (s), 137.5 (s), 140.2 (s), 148.8 (s), 151.5 (s); MS *m/z* (rel intensity) 333 ($M^+$+3; 6), 332 ($M^+$+2; 42), 331 ($M^+$+1; 12), 330 ($M^+$; 43), 263 (37), 261 (38), 174 (37), 158 (14), 156 (12), 91 (100), 78 (16). Found: *m/z* 329.9971. Calcd for $C_{13}H_{10}BrF_3N_2$: M, 329.9980.

**5-Bromo-2-[4-ethylbenzyl(trifluoromethyl)amino]pyridine (8g).** Yield: 41%. A colorless oil, bp 210 °C/0.7 mmHg; $R_f$ = 0.76 (hexane : $Et_2O$ = 10 : 1). IR 2967, 1584, 1559, 1479, 1377, 1319, 1269, 1190, 1109, 1101, 819 cm$^{-1}$; $^1$H NMR (200 MHz) $\delta$ = 1.21 (t, $J$ = 8 Hz, 3 H), 2.61 (q, $J$ = 8 Hz, 2 H), 4.98 (q, $J$ = 1 Hz, 2 H), 6.97 (dd, $J$ = 1, 9 Hz, 1 H), 7.09—7.22 (m, 4 H), 7.68 (dd, $J$ = 3, 9 Hz, 1 H), 8.36 (dd, $J$ = 1, 3 Hz, 1 H); $^{19}$F NMR (188 MHz) $\delta$ = −55.77 (m); $^{13}$C NMR (50.3 MHz) $\delta$ = 15.4 (s), 28.4 (s), 48.2 (q, $J$ = 2 Hz), 112.7 (q, $^{1}J_{C-F}$ = 258 Hz), 113.7 (s), 114.6 (s), 127.1 (s), 127.9 (s), 134.7 (br), 140.1 (s), 143.3 (s), 148.7 (s), 151.5 (s); MS *m/z* (rel intensity) 359 ($M^+$+1; 15), 358 ($M^+$; 88), 357 ($M^+$−1; 19), 356 ($M^+$−2; 89), 289 (42), 287 (43), 277 (5), 200 (73), 159 (28), 158 (39), 157 (27), 156 (37), 130 (15), 118 (79), 117 (100), 116 (42), 115 (99), 102 (21), 91 (98), 78 (50), 77 (35), 69 (54). Found: C, 50.11; H, 4.11; N, 7.83%. Calcd for $C_{15}H_{14}BrF_3N_2$: C, 50.16; H, 3.93; N, 7.80%.

**5-Bromo-2-{[4-(1-fluoroethyl)benzyl](trifluoromethyl)amino}pyridine (8g′).** Yield: 38%. A colorless oil, bp 220 °C/0.7 mmHg; $R_f$ = 0.63 (hexane : $Et_2O$ = 10 : 1). IR 2984, 2934, 2361, 1912, 1582, 1563, 1474, 1379, 1321, 1271, 1244, 1192, 1109, 1069, 1010, 1000, 820 cm$^{-1}$; $^1$H NMR (200 MHz) $\delta$ = 1.61 (dd, $J$ = 6, 24 Hz, 3 H), 5.01 (br, 2 H), 5.69 (dq, $J$ = 6, 48 Hz, 1 H), 7.01 (dd, $J$ = 1, 9 Hz, 1 H), 7.09—7.22 (m, 4 H), 7.69 (dd, $J$ = 3, 9 Hz, 1 H), 8.36 (dd, $J$ = 1, 3 Hz, 1 H); $^{19}$F NMR (188 MHz) $\delta$ = −55.83 (br, 3 F), −167.12 (dd, $J$ = 24, 48 Hz, 1 F); $^{13}$C NMR (50.3 MHz) $\delta$ = 22.8 (d, $J$ = 25 Hz), 48.5 (q, $J$ = 2 Hz), 90.7 (d, $^{1}J_{C-F}$ = 168 Hz), 113.8 (s), 114.3 (q, $J$ = 4.2 Hz), 122.6 (q, $^{1}J_{C-F}$ = 258 Hz), 125.4 (d, $J$ = 8 Hz), 127.2 (s), 137.6 (m), 140.1 (s), 140.2 (s), 140.7 (s), 148.8 (s), 151.4 (s); MS *m/z* (rel intensity) 378 ($M^+$+2; 9), 377 ($M^+$+1; 2), 376 ($M^+$; 9), 375 ($M^+$−1; 1), 338 (3), 336 (3), 309 (13), 307 (10), 289 (5), 287 (5), 220 (18), 200 (11), 185 (6), 159 (10), 158 (20), 137 (86), 122 (24), 117 (100), 115 (62), 91 (40), 89 (12), 78 (36), 77 (18), 76 (26), 69 (28), 65 (22), 64 (14). Found: C, 47.56; H, 3.45; N, 7.67%. Calcd for $C_{15}H_{13}BrF_4N_2$: C, 47.77; H, 3.47; N, 7.43%.

**5-Bromo-2-[methyl(trifluoromethyl)amino]pyrimidine (12a).** Yield: 84%. Colorless needles, mp 60.8—61.5 °C; $R_f$ = 0.52 (hexane : EtOAc = 10 : 1). IR (KBr) 1579, 1544, 1486, 1467, 1414, 1373, 1319, 1253, 1177, 1138, 1118, 1089, 942, 922, 789, 779, 616 cm$^{-1}$; $^1$H NMR (200 MHz) $\delta$ = 3.34 (q, $J$ = 2 Hz, 3 H), 8.54 (s, 2 H); $^{19}$F NMR (188 MHz) $\delta$ = −57.4 (s); $^{13}$C NMR (50.3 MHz) $\delta$ = 31.8 (s), 111.9 (s), 121.7 (q, $J$ = 259 Hz), 157.6 (s), 158.0 (s); MS *m/z* (rel intensity) 257 ($M^+$+2; 69), 255 ($M^+$; 71), 188 (55), 186 (56), 160 (98), 158 (100), 133 (12), 131 (13), 106 (15), 104 (13), 79 (28). Found: *m/z* 254.9647. Calcd for $C_6H_5BrF_3N_3$: M, 254.9619.

**5-Bromo-2-[propyl(trifluoromethyl)amino]pyrimidine (12b).** Yield: 81%. A colorless oil; $R_f$ = 0.70 (hexane : EtOAc = 10 : 1). IR (KBr) 3060, 2969, 1572, 1543, 1474, 1464, 1433, 1393, 1377, 1333, 1310, 1235, 1206, 1180, 1146, 1088, 959, 791 cm$^{-1}$; $^1$H NMR (300 MHz) $\delta$ = 0.93 (t, $J$ = 8 Hz, 3 H), 1.68 (sextet, $J$ = 8 Hz, 2 H), 3.80 (qt, $J$ = 2, 8 Hz, 2 H), 8.53 (s, 2 H); $^{19}$F NMR (188 MHz) $\delta$ = −56.33 (s); $^{13}$C NMR (75.5 MHz) $\delta$ = 10.9 (s), 21.8 (s), 46.9 (s), 111.6 (s), 121.8 (q, $J$ = 260 Hz), 157.3 (s), 158.1 (s); MS *m/z* (rel intensity) 285 ($M^+$+2; 62), 283 ($M^+$; 53), 256 (86), 254 (100), 243 (27), 241 (29), 224 (22), 223 (75), 222 (21), 221 (84), 216 (15), 214 (12), 205 (14), 204 (11), 186 (12), 174 (13), 172 (14), 160 (29), 159 (62), 158 (27), 157 (57), 120 (14), 119 (13), 106 (16), 105 (20), 91 (18), 83 (21), 78 (76), 69 (80). Found: *m/z* 282.9923. Calcd for $C_8H_9BrF_3N_3$: M, 282.9932.

**5-Bromo-2-[hexyl(trifluoromethyl)amino]pyrimidine (12c).** Yield: 61%. A colorless oil; $R_f$ = 0.54 (hexane : $Et_2O$ = 20 : 1). IR 2960, 2933, 2873, 2861, 1575, 1543, 1472, 1433, 1395, 1381, 1325, 1298, 1245, 1225, 1206, 1194, 1175, 1143, 1089, 792, 637 cm$^{-1}$; $^1$H NMR (200 MHz) $\delta$ = 0.89 (t, $J$ = 7 Hz, 3 H), 1.31—1.43 (m, 6 H), 1.61—1.67 (m, 2 H), 3.77—3.88 (m, 2 H), 8.53 (s, 2 H); $^{19}$F NMR (188 MHz) $\delta$ = −56.2 (t, $J$ = 2 Hz); $^{13}$C NMR (50.3 MHz) $\delta$ = 13.9 (s), 22.5 (s), 26.2 (s), 28.5 (s), 31.4 (s), 45.4 (s), 111.6 (s), 121.8 (q, $^{1}J_{C-F}$ = 259 Hz), 157.2 (s), 158.1 (s); MS *m/z* (rel intensity) 327 ($M^+$+2; 7), 326 ($M^+$+1; 53), 325 ($M^+$; 8), 324 ($M^+$−1; 54), 285 (19), 283 (19), 270 (11), 268 (11), 255 (100), 253 (99), 243 (20), 241 (20), 223 (59), 221 (56), 187 (13), 185 (12), 159 (51), 157 (46), 78 (33). Found: *m/z* 325.0382. Calcd for $C_{11}H_{15}BrF_3N_3$: M, 325.0402.

**5-Bromo-2-[octyl(trifluoromethyl)amino]pyrimidine (12d).**

Yield: 24% along with **11d** (62% yield). A colorless oil; $R_f = 0.91$ (hexane : $Et_2O$ = 10 : 1). IR 2929, 2858, 1575, 1543, 1472, 1432, 1395, 1380, 1325, 1300, 1250, 1233, 1208, 1183, 1144, 1089, 935, 806, 792, 637 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta = 0.88$ (t, $J = 7$ Hz, 3 H), 1.27—1.43 (m, 10 H), 1.58—1.63 (m, 2 H), 3.76—3.87 (m, 2 H), 8.52 (s, 2 H); $^{19}F$ NMR (188 MHz) $\delta = -56.2$ (t, $J = 2$ Hz); $^{13}C$ NMR (50.3 MHz) $\delta = 14.0$ (s), 22.6 (s), 26.5 (s), 28.5 (s), 29.1 (s), 31.8 (s), 45.5 (s), 111.6 (s), 121.8 (q, $^1J_{C-F} = 260$ Hz), 157.2 (s), 158.1 (s); MS *m/z* (rel intensity) 355 ($M^+$+2; 10), 354 ($M^+$+1; 64), 353 ($M^+$; 11), 352 ($M^+-1$; 66), 325 (5), 323 (5), 285 (23), 283 (23), 255 (100), 253 (99), 243 (21), 241 (20), 223 (59), 221 (57), 159 (51), 157 (45), 78 (32). Found: *m/z* 353.0716. Calcd for $C_{13}H_{19}BrF_3N_3$: M, 353.0715.

**5-Bromo-2-[dodecyl(trifluoromethyl)amino]pyrimidine (12e).** Yield: 15% along with **11e** (65% yield). A colorless oil; $R_f = 0.71$ (hexane : $Et_2O$ = 10 : 1). IR (KBr) 2981, 2956, 2916, 2874, 2849, 1575, 1547, 1467, 1427, 1381, 1331, 1245, 1227, 1141, 791, 639 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta = 0.88$ (t, $J = 7$ Hz, 3 H), 1.17—1.30 (m, 18 H), 1.56—1.67 (m, 2 H), 3.76—3.87 (m, 2 H), 8.52 (s, 2 H); $^{19}F$ NMR (188 MHz) $\delta = -56.2$ (t, $J = 2$ Hz); $^{13}C$ NMR (50.3 MHz) $\delta = 14.1$ (s), 22.7 (s), 26.5 (s), 28.5 (s), 29.2 (s), 29.3 (s), 29.6 (s), 31.9 (s), 45.5 (s), 111.6 (s), 121.8 (q, $^1J_{C-F} = 260$ Hz), 157.3 (s), 158.1 (s); MS *m/z* (rel intensity) 412 ($M^+$+3; 20), 411 ($M^+$+2; 99), 410 ($M^+$+1; 22), 409 ($M^+$; 100), 325 (5), 323 (5), 285 (22), 283 (23), 255 (89), 254 (88), 224 (46), 223 (52), 222 (48), 221 (48), 187 (9), 185 (8), 160 (16), 159 (42), 158 (17), 157 (35). Found: *m/z* 409.1335. Calcd for $C_{17}H_{27}BrF_3N_3$: M, 409.1341.

**Synthesis of 3-[Benzyl(trifluoromethyl)amino]pyridine (7h).** This compound was produced from **6h** in 82% yield as a colorless oil through a similar procedure to that for the preparation of **4**. $R_f = 0.45$ (hexane : $Et_2O$ = 1 : 1). IR 3066, 3036, 2931, 1733, 1590, 1575, 1482, 1455, 1424, 1376, 1266, 1230, 1195, 1104, 1080, 1064, 1037, 994, 911, 813, 739, 713, 700, 650 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta = 4.57$ (s, 2 H), 7.17—7.33 (m, 7 H), 7.47 (dm, $J = 8$ Hz, 1 H), 8.40—8.44 (m, 1 H); $^{19}F$ NMR (188 MHz) $\delta = -58.00$ (s); $^{13}C$ NMR (50.3 MHz) $\delta = 53.0$ (s), 123.0 (q, $^1J_{C-F} = 256$ Hz), 123.6 (s), 127.8 (s), 128.0 (s), 128.6 (s), 133.0 (s), 135.9 (s), 137.4 (s), 147.5 (s), 147.6 (s); MS *m/z* (rel intensity) 252 ($M^+$; 19), 92 (14), 91 (100), 78 (4). Found: *m/z* 252.0857. Calcd for $C_{13}H_{11}F_3N_2$: M, 252.0874.

**Bromination of 2-[Benzyl(trifluoromethyl)amino]pyridine (7f).** A solution of bromine (0.176 g, 1.1 mmol) in dichloromethane (1.2 mL) was added dropwised to a stirred solution of $TBAH_2F_3$ (0.30 g, 1.0 mmol) and **7f** (0.126 g, 0.50 mmol) in dichloromethane (1.0 mL) at room temperature. The reaction mixture was heated to reflux for 1.5 h, and the whole mixture was treated with aqueous $NaHSO_3$/$NaHCO_3$/NaOH (pH 10) solution. The organic phase was separated, and the aqueous phase was extracted with diethyl ether three times. The combined organic phase was dried over sodium sulfate, filtered through a pad of Celite/silica gel (Wako Gel C-100), and concentrated under reduced pressure. The residue was purified by column chromatography to give **7f** (16 mg) and **8f** (0.139 g) in 14% and 84% yield, respectively.

**Reaction of 4m, 8a, or 12a with *p*-Bromobenzaldehyde.** A solution of *n*-BuLi in hexane (1.6 M, 0.60 mmol) was added dropwise to a stirred solution of bromoaryl(trifluoromethyl)amine **4m**, **8a**, or **12a** (0.50 mmol) in THF (2.0 mL) at −78 °C. The resulting mixture was stirred for 30 min at −78 °C before a treatment with a solution of 4-bromobenzaldehyde (0.70 mmol) in THF (1.0 mL). The reaction mixture was slowly warmed up to room temperature, stirred for 12 h, poured into a sat. $NaHCO_3$ aq solution, and extracted with diethyl ether three times. The combined organic layer was dried over sodium sulfate, filtered, and concentrated under reduced pressure. Purification by column chromatography gave the desired adduct **21**, **22**, or **23**, respectively. The yields and spectra of the products are summarized below.

**(4- Bromophenyl){4- [methyl(trifluoromethyl)amino]phenyl}methanol (16).** Yield: 69%. A colorless oil; $R_f = 0.23$ (hexane : EtOAc = 5 : 1). IR 3280, 2977, 2872, 1790, 1700, 1651, 1514, 1374, 1276, 1113, 1071, 1011, 857, 731 $cm^{-1}$; $^1H$ NMR (300 MHz) $\delta = 2.74$ (br s, 1 H), 3.14 (q, $J = 1$ Hz, 3 H), 5.87 (s, 1 H), 7.33 (d, $J = 8$ Hz, 2 H), 7.36 (d, $J = 8$ Hz, 2 H), 7.43 (d, $J = 8$ Hz, 2 H), 7.58 (d, $J = 8$ Hz, 2 H); $^{19}F$ NMR (282 MHz) $\delta = -60.9$ (s); $^{13}C$ NMR (75.5 MHz) $\delta = 36.1$ (q, $J = 2$ Hz), 75.1 (s), 121.5 (s), 123.3 (q, $^1J_{C-F} = 256$ Hz), 124.7 (q, $J = 2$ Hz), 127.2 (s), 128.1 (s), 131.6 (s), 141.0 (s), 142.2 (s), 142.4 (s); MS *m/z* (rel intensity) 361 ($M^+$+2; 11), 359 ($M^+$; 8), 254 (10), 204 (22), 203 (18), 202 (76), 185 (50), 183 (37), 176 (62), 165 (43), 156 (65), 105 (30), 77 (100), 69 (40). Found: *m/z* 359.0133. Calcd for $C_{15}H_{13}^{79}BrF_3NO$: M, 359.0133.

**(4-Bromophenyl){6-[methyl(trifluoromethyl)amino]-3-pyridyl}methanol (17).** This compound was obtained in 78% as a colorless oil. $R_f = 0.37$ (hexane : $Et_2O$ = 1 : 1). IR 3373, 2358, 2341, 1607, 1574, 1490, 1398, 1353, 1257, 1199, 1125, 1072, 1011, 824, 735 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta = 2.27$ (d, $J = 4$ Hz, 1 H), 3.25 (q, $J = 2$ Hz, 3 H), 5.80 (d, $J = 4$ Hz, 1 H), 7.02—7.09 (m, 1 H), 7.21—7.28 (m, 2 H), 7.14—7.58 (m, 3 H), 8.32 (d, $J = 2$ Hz, 1 H); $^{19}F$ NMR (188 MHz) $\delta = -57.8$ (dq, $J = 2$, 2 Hz); $^{13}C$ NMR (50.3 MHz) $\delta = 32.3$ (s), 72.9 (s), 113.5 (s), 121.7 (s), 122.7 (q, $^1J_{C-F} = 257$ Hz), 128.0 (s), 131.7 (s), 133.6 (s), 136.3 (s), 142.0 (s), 146.1 (s), 153.2 (s); MS *m/z* (rel intensity) 362 ($M^+$+2; 38), 360 ($M^+$; 41), 345 (5), 343 (10), 293 (33), 291 (34), 266 (10), 265 (17), 264 (13), 263 (17), 205 (37), 203 (100), 185 (36), 183 (30), 157 (72), 106 (17), 92 (12), 77 (59). Found: *m/z* 360.0073. Calcd for $C_{14}H_{12}BrF_3N_2O$: M, 360.0086.

**(4-Bromophenyl){2-[methyl(trifluoromethyl)amino]-5-pyrimidyl}methanol (18).** Yield: 82%. A colorless powder, mp 67.8—69.4 °C; $R_f = 0.41$ (hexane : $Et_2O$ = 1 : 2). IR (KBr) 3374, 2960, 2931, 2894, 2873, 1602, 1560, 1485, 1415, 1377, 1324, 1260, 1180, 1130, 1092, 1072, 1049, 1011, 805, 735, 618 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta = 2.38$ (br s, 1 H), 3.35 (q, $J = 2$ Hz, 3 H), 5.79 (s, 1 H), 7.22—7.27 (m, 2 H), 7.49—7.53 (m, 2 H), 8.47 (d, $J = 1$ Hz, 2 H); $^{19}F$ NMR (188 MHz) $\delta = -57.2$ (q, $J = 2$ Hz); $^{13}C$ NMR (50.3 MHz) $\delta = 31.6$ (s), 71.2 (s), 121.9 (q, $J = 259$ Hz), 122.0 (s), 128.0 (s), 129.7 (s), 131.9 (s), 141.4 (s), 156.3 (s), 158.4 (s); MS *m/z* (rel intensity) 363 ($M^+$+2; 34), 361 ($M^+$; 41), 346 (9), 344 (10), 294 (17), 292 (16), 266 (19), 264 (21), 206 (39), 204 (100), 185 (21), 183 (16), 158 (48), 77 (46). Found: *m/z* 361.0042. Calcd for $C_{13}H_{11}BrF_3N_3O$: M, 361.0038.

**Carboxylation of Bromoaryl(methyl)(trifluoromethyl)amines.** A hexane solution of *n*-BuLi (1.6 M, 0.59 mmol) was slowly added to a stirred solution of **4m**, **8a**, or **12a** (0.47 mmol) in THF (1.0 mL) at −78 °C. The resulting mixture was stirred for 30 min at −78 °C, and carbon dioxide was bubbled into the mixture. The reaction mixture was warmed to room temperature for over 30 min during $CO_2$ bubbling, then treated with water (ca. 0.04 mL) and MeOH (0.4 mL), and stirred for 10 min at room temperature before a treatment with a 10% hexane solution of trimethylsilyldiazomethane (0.94 mmol). The resulting mixture was stirred for 30 min at room temperature, poured into a sat. $NaHCO_3$ aq solution, and extracted with diethyl ether three times. The combined organic layer was dried over sodium sulfate, filtered, and concentrated under reduced pressure. Purification by flash column chromatography gave **19**, **20**, or **21**. The yields and spectroscopic properties of the

products are given below.

**Methyl 4- [Methyl(trifluoromethyl)amino]benzoate (19).** Yield: 98%. A colorless oil; $R_f = 0.45$ (hexane : $Et_2O$ = 10 : 1). IR 2998, 2955, 2847, 1728, 1613, 1518, 1437, 1345, 1287, 1200, 1148, 1117, 1063, 1019, 774, 706 $cm^{-1}$; $^1H$ NMR (300 MHz) $\delta$ = 3.12 (q, $J$ = 1 Hz, 3 H), 3.91 (s, 3 H), 7.23 (d, $J$ = 9 Hz, 2 H), 8.01 (d, $J$ = 9 Hz, 2 H); $^{19}F$ NMR (282 MHz) $\delta$ = −59.44 (s); $^{13}C$ NMR (75.5 MHz) $\delta$ = 35.4 (q, $J$ = 2 Hz), 52.1 (s), 121.8 (q, $J$ = 2 Hz), 122.8 (q, $J$ = 257 Hz), 126.3 (s), 130.6 (s), 146.6 (s), 166.4 (s); MS *m/z* (rel intensity) 234 ($M^+$+1; 5), 233 ($M^+$; 41), 214 (13), 203 (11), 202 (100), 154 (11), 132 (12), 105 (19), 104 (19), 90 (12), 77 (32), 69 (26), 63 (21). Found: *m/z* 233.0664. Calcd for $C_{10}H_{10}F_3NO_2$: M, 233.0664.

**Methyl 2-[Methyl(trifluoromethyl)amino]pyridine-5-carboxylate (20).** This ester was prepared in 45% yield from **8a** as a colorless oil by a procedure similar to that of **19** expect for treatment of solid $CO_2$ and an ethereal solution of trimethylsilyl diazomethane (excess). $R_f = 0.44$ (hexane : $Et_2O$ = 5 : 1). IR 2958, 1730, 1607, 1573, 1497, 1436, 1393, 1357, 1330, 1297, 1276, 1199, 1126, 1072, 1020, 782 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta$ = 3.35 (q, $J$ = 2 Hz, 3 H), 3.92 (s, 3 H), 7.09 (dm, $J$ = 9 Hz, 1 H), 8.17 (dd, $J$ = 3, 9 Hz, 1 H), 8.94 (dd, $J$ = 1, 3 Hz, 1 H); $^{19}F$ NMR (188 MHz) $\delta$ = −57.1 (dq, $J$ = 2, 2 Hz); $^{13}C$ NMR (50.3 MHz) $\delta$ = 31.8 (s), 52.1 (s), 111.2 (s), 120.0 (s), 122.3 (q, $J$ = 258 Hz), 138.6 (s), 150.0 (s), 156.2 (s), 165.6 (s); MS *m/z* (rel intensity) 235 ($M^+$+1; 4), 234 ($M^+$; 41), 215 (10), 214 (18), 203 (33), 165 (100), 148 (27), 137 (82), 106 (27), 78 (25). Found: *m/z* 234.0661. Calcd for $C_9H_9F_3N_2O_2$: M, 234.0662.

**Methyl 2-[Methyl(trifluoromethyl)amino]pyrimidine-5-carboxylate (21).** Yield: 78%. A colorless solid, mp 110.5—111.8 °C; $R_f = 0.32$ (hexane : $Et_2O$ = 5 : 1). IR 3056, 2965, 1719, 1607, 1553, 1497, 1418, 1399, 1320, 1254, 1196, 1136, 1092, 951, 808 $cm^{-1}$; $^1H$ NMR (300 MHz) $\delta$ = 3.44 (q, $J$ = 2 Hz, 3 H), 3.95 (s, 3 H), 9.06 (s, 2 H); $^{19}F$ NMR (282 MHz) $\delta$ = −57.07 (q, $J$ = 2 Hz); $^{13}C$ NMR (75.5 MHz) $\delta$ = 31.7 (q, $J$ = 2 Hz), 52.2 (s), 117.4 (s), 121.4 (q, $J$ = 261 Hz), 159.3 (s), 160.8 (s), 164.2 (s); MS *m/z* (rel intensity) 236 ($M^+$+1; 6), 235 ($M^+$; 47), 216 (16), 204 (48), 166 (78), 149 (14), 139 (17), 138 (100), 107 (12), 80 (28), 79 (18), 69 (52). Found: *m/z* 235.0571. Calcd for $C_8H_8F_3N_3O_2$: M, 235.0569.

**Synthesis of 6-Chloro-9-benzyl-9*H*-purine (23).** A solution of 6-chloropurine (**22**, 0.31 g, 2.0 mmol) in DMF (2.0 mL) was added dropwise to a stirred suspension of NaH (60% dispersion in mineral oil, 53 mg, 2.2 mmol) in DMF (1.0 mL) at 0 °C. The reaction mixture was stirred at room temperature for 1 h and then cooled to 0 °C. Benzyl bromide (0.48 mL, 4.0 mmol) was added dropwise at 0 °C, and the whole mixture was stirred at room temperature for 3 h before quenching with a sat. $NaHCO_3$ aq solution and extraction with diethyl ether three times. The combined organic phase was dried over sodium sulfate, filtered through a pad of Celite/silica gel (Wako Gel C-100), and concentrated. The residue was purified by flash column chromatography ($CH_2Cl_2$ : MeOH = 25 : 1) to give **23** (0.34 g) and 6-chloro-7-benzylpurine (**23′**, 0.130 g) in 69% and 27% yield, respectively.

**6-Chloro-9-benzyl-9*H*-purine (23).** A white powder, mp 80.5—81.9 °C; $R_f = 0.41$ ($CH_2Cl_2$ : MeOH = 10 : 1). IR 3102, 3063, 3006, 1919, 1821, 1597, 1559, 1497, 1447, 1453, 1397, 1385, 1345, 1244, 1211, 1179, 1146, 1121, 953, 938, 858, 725 $cm^{-1}$; $^1H$ NMR (200 MHz) $\delta$ = 5.69 (s, 2 H), 7.15—7.22 (m, 2 H), 7.36—7.45 (m, 3 H), 8.22 (s, 1 H), 8.90 (s, 1 H); $^{13}C$ NMR (75.5 MHz) $\delta$ = 47.5 (s), 127.6 (s), 128.4 (s), 128.8 (s), 131.1 (s), 134.3 (s), 144.9 (s), 150.5 (s), 151.5 (s), 151.7 (s); MS *m/z* (rel intensity) 246 ($M^+$+2; 11), 245 ($M^+$+1; 20), 244 ($M^+$; 34), 243 ($M^+$−1; 48), 182 (9), 92 (9), 91 (100), 65 (36). Found: *m/z* 244.0517. Calcd for $C_{12}H_9ClN_4$: M, 244.0516.

**6-Chloro-7-benzylpurine (23′).** A white powder, mp 141.9—143.3 °C; $R_f = 0.38$ ($CH_2Cl_2$ : MeOH = 10 : 1). IR 3030, 1603, 1537, 1483, 1456, 1395, 1367, 1335, 1287, 1169, 1075, 968, 743 $cm^{-1}$; $^1H$ NMR (300 MHz) $\delta$ = 5.71 (s, 2 H), 7.15—7.23 (m, 2 H), 7.36—7.45 (m, 3 H), 8.26 (s, 1 H), 8.90 (s, 1 H); $^{13}C$ NMR (75.5 MHz) $\delta$ = 50.7 (s), 122.5 (s), 127.0 (s), 128.9 (s), 129.3 (s), 134.5 (s), 143.2 (s), 149.1 (s), 152.6 (s), 161.9 (s); MS *m/z* (rel intensity) 247 ($M^+$+3; 1), 246 ($M^+$+2; 8), 245 ($M^+$+1; 6), 244 ($M^+$; 24), 243 ($M^+$−1; 9), 92 (8), 91 (100), 65 (22). Found: *m/z* 244.0515. Calcd for $C_{12}H_9ClN_4$: M, 244.0516.

**Synthesis of 6-Methylamino-9-benzyl-9*H*-purine (24).** Triethylamine (1.8 mL, 12.8 mmol) was added dropwise to a stirred solution of **23** (1.05 g, 4.3 mmol) and methylamine hydrochloride (1.49 g, 22.0 mmol) in dichloromethane (5.0 mL) at room temperature. The reaction mixture was stirred at room temperature for 12 d. Quenching with a sat. $NaHCO_3$ aq solution, extraction with diethyl ether three times, followed by purification by flash column chromatography ($CH_2Cl_2$ : MeOH = 20 : 1), gave **24** (0.95 g, 93% yield) as a colorless oil. $R_f = 0.33$ ($CH_2Cl_2$ : MeOH = 20 : 1). IR 3249, 3067, 1624, 1588, 1514, 1451, 1418, 1298, 1254, 1190, 729 $cm^{-1}$; $^1H$ NMR (300 MHz) $\delta$ = 3.20 (br s, 3 H), 5.37 (s, 2 H), 6.30 (br s, 1 H), 7.25—7.38 (m, 5 H), 7.72 (s, 1 H), 8.46 (s, 1 H); $^{13}C$ NMR (75.5 MHz) $\delta$ = 27.5 (m), 47.0 (s), 50.7 (s), 119.7 (s), 127.6 (s), 128.3 (s), 128.9 (s), 135.6 (s), 139.4 (s), 152.1 (s), 153.3 (s), 155.5 (s); MS *m/z* (rel intensity) 240 ($M^+$+1; 11), 239 ($M^+$; 67), 238 ($M^+$−1; 66), 209 (10), 148 (59), 119 (11), 92 (11), 91 (100), 65 (40). Found: *m/z* 239.1162. Calcd for $C_{13}H_{13}N_5$: M, 239.1171.

**Ethyl *N*-(9-Benzyl-9*H*-purine-6-yl)-*N*-methyldithiocarbamate (25).** A hexane solution of *n*-BuLi (1.6 M, 0.20 mL, 0.33 mmol) was added dropwise to a solution of **24** (72 mg, 0.30 mmol) in THF (2.0 mL) at −78 °C. The reaction mixture was slowly warmed up to 0 °C in 1 h and then slowly treated with a solution of ethyl chlorodithioformate (81 mg, 0.60 mmol) in THF (1.5 mL) at 0 °C. The resulting mixture was stirred at room temperature for 2 h, and poured into a sat. $NaHCO_3$ aq solution. After the aqueous phase was extracted with diethyl ether three times, the combined organic phase was dried over sodium sulfate, filtered, and concentrated. The residue was purified by flash column chromatography (hexane : $Et_2O$ : EtOAc = 1 : 1 : 1) to give **25** (39 mg, 37% yield) as a brown oil. $R_f = 0.43$ (hexane : $Et_2O$ : EtOAc = 1 : 1 : 1). IR 3067, 2969, 2929, 2870, 1595, 1499, 1456, 1406, 1244, 1154, 1096, 1038, 1003, 725, 698 $cm^{-1}$; $^1H$ NMR (300 MHz) $\delta$ = 1.30 (t, $J$ = 8 Hz, 3 H), 3.27 (q, $J$ = 8 Hz, 2 H), 3.95 (s, 3 H), 5.48 (s, 2 H), 7.28—7.40 (m, 5 H), 8.11 (s, 1 H), 8.94 (s, 1 H); $^{13}C$ NMR (75.5 MHz) $\delta$ = 13.0 (s), 32.0 (s), 43.0 (s), 47.7 (s), 127.0 (s), 127.2 (s), 128.0 (s), 128.8 (s), 129.2 (s), 134.6 (s), 144.7 (s), 152.3 (s), 153.9 (s), 200.9 (s); MS *m/z* (rel intensity) 345 ($M^+$+2; 0.7), 344 ($M^+$+1; 1), 343 ($M^+$; 7), 314 (16), 268 (6), 209 (7), 148 (5), 91 (100), 65 (18). Found: *m/z* 343.0926. Calcd for $C_{16}H_{17}N_5S_2$: M, 343.0925.

**6-[Methyl(trifluoromethyl)amino]-9-benzyl-9*H*-purine (26).** To a stirred solution of $TBAH_2F_3$ (0.24 g, 0.79 mmol) and dithiocarbamate **25** (54 mg, 0.157 mmol) in $CH_2Cl_2$ (0.5 mL) was added DBH (0.180 g, 0.63 mmol) in one portion at 0 °C. The resulting mixture was stirred for 1 h at 0 °C, then poured into a $NaHSO_3$/$NaHCO_3$/NaOH aq solution (pH 10) and extracted with diethyl ether three times. The combined organic phase was dried over anhydrous sodium sulfate, filtered through a pad of Celite/silica gel (Wako Gel C-100), and concentrated. The residue was purified by column chromatography (hexane : $Et_2O$ = 1 : 1) to give **26** (12 mg, 25% yield) as colorless needles; mp 89.6—90.9 °C; $R_f = 0.67$ ($Et_2O$). IR 2926, 2853, 1730, 1590, 1582, 1476, 1458, 1433, 1364,

1296, 1237, 1211, 1154, 1121, 1075, 731, 718 $cm^{-1}$; $^1H$ NMR (300 MHz) $\delta = 3.73$ (q, $J = 2$ Hz, 3 H), 5.43 (s, 2 H), 7.23—7.40 (m, 5 H), 7.94 (s, 1 H), 8.68 (s, 1 H); $^{19}F$ NMR (188 MHz) $\delta = -57.7$ (q, $J = 2$ Hz); $^{13}C$ NMR (75.5 MHz) $\delta = 33.6$ (q, $J = 2$ Hz), 47.3 (s), 121.6 (q, $J = 261$ Hz), 125.1 (s), 127.8 (s), 128.1 (s), 128.6 (s), 129.1 (s), 135.1 (s), 141.5 (s), 151.6 (s), 152.4 (s); MS *m/z* (rel intensity) 308 ($M^+$+1; 3), 307 ($M^+$; 19), 306 ($M^+-1$; 7), 210 (9), 119 (9), 92 (9), 91 (100), 69 (7), 65 (27). Found: *m/z* 307.1049. Calcd for $C_{14}H_{12}F_3N_5$: M, 307.1045.

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