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A facile preparation of *trans*-1,2-cyclopropanes containing *p*-trifluoromethylphenyl group and its application to the construction of pyrazole and cyclopropane ring fused pyridazinone derivatives

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ABSTRACT

A facile methodology for the preparation of highly functionalized *trans*-1,2-cyclopropanes containing *p*-trifluoromethylphenyl group **3** is described. Arsonium bromides **1** reacted with electron-deficient olefins **2** in the presence of K_2CO_3 to provide **3** stereoselectively in moderate to good yields. This process has been successfully applied to the construction of cyclopropane ring fused pyridazinone derivatives **4** or pyrazole derivatives **5**.

1. Introduction

The synthesis and application of multisubstituted cyclopropanes have been a subject of great interest due to their roles as the basic structural elements in a wide range of biologically active compounds and important intermediates in organic synthesis.[1] On the other hand, it is well accepted that selective introduction of fluorine-containing functionality to organic compounds often causes marked effects on their physical and chemical properties,[2] and these effects can make them suitable for diverse applications in synthetic, agricultural, and medicinal chemistry as well as in material science.[3] It is therefore still of importance to develop simple and effective methods for the synthesis of cyclopropanes with fluorine-containing group.[4]

The tandem Michael addition–elimination of ylides to electron-deficient alkenes provides easy access to functionalized cyclopropanes.[5] Among the ylides reported, arsonium ylides are known for their high reactivity and high diastereoselectivity in alkene, epoxide, and cyclopropane formation.[6] They have similar reactivity to the telluronium ylides, and in general exhibit higher diastereoselectivities than the latter. Moreover, the stability of triphenyl arsine in air may facilitate the experimental operations. Continuing our efforts toward the stereoselective synthesis and application of cyclopropanes,[7] we focused on an arsonium ylide-based stereoselective synthesis of *trans*-cyclopropanes with *p*-trifluoromethylphenyl group, which can further be transformed into pyrazole and cyclopropane ring fused pyridazinone derivatives with potential biological activities.[8,9]

2. Results and discussion

In the presence of K_2CO_3, arsonium bromides **1** reacted with electron-deficient olefins **2** in chloroform at room temperature for the time indicated in Table 1 to give cyclopropanes **3** in moderate to good yields (Scheme 1).

In the beginning, the stereochemistry of compounds **3a–h** was deduced from their ^{19}F and ^{1}H NMR spectra. For example, the ^{19}F NMR spectrum of **3a** showed a peak at −63.1 ppm (s, $-CF_3$), indicating one sole product with *p*-trifluoromethylphenyl group was obtained. In addition, the ^{1}H NMR spectrum of compound **3a** showed two doublets at 3.16 ppm (J=8.0 Hz, 1H) and 3.76 ppm (J=8.0 Hz, 1H) assigned to be the two cyclopropyl protons. The ^{19}F

Table 1
Preparation of *cis*-1,2-cyclopropanes with arsonium bromide **1** and olefin **2**

Entry	R_1	R_2	Product **3**	Time (h)	Yield[a] (%)
1	–CN	–CN	**3a**	12	50
2	–C(O)Ph	–CN	**3b**	10	67
3	–C(O)(furan-2-yl)	–CN	**3c**	7	77
4	–C(O)(thiophen-2-yl)	–CN	**3d**	5	80
5	–C(O)Ph	$-C(O)OCH_3$	**3e**	6	78
6	–C(O)(furan-2-yl)	$-C(O)OCH_3$	**3f**	6	81
7	–C(O)(thiophen-2-yl)	$-C(O)OCH_3$	**3g**	6	90
8	–Ph	$-C(O)OCH_3$	**3h**	6	67

[a] Isolated yield.

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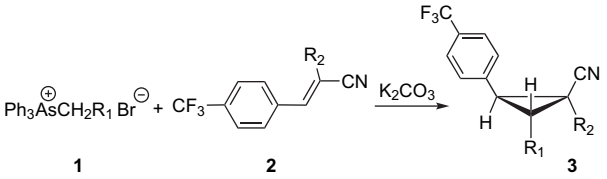
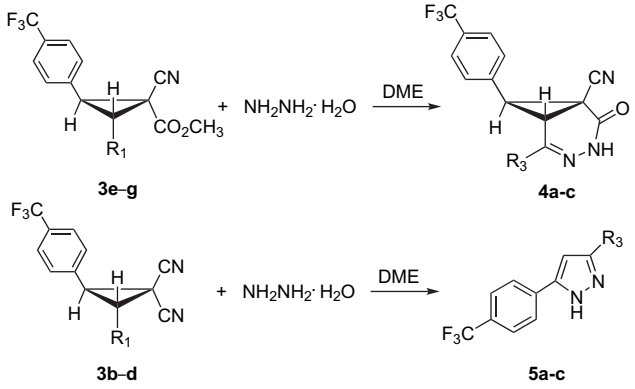


Scheme 1.

and ^{1}H NMR spectra of compounds **3b**–**h** manifested themselves in a similar manner. In all of compounds **3a**–**h**, the coupling constant of the two vicinal cyclopropyl protons (J=8.0–9.0 Hz) indicated a trans configuration.[10] Furthermore, we treated the supposed *trans*-1,2-cyclopropanes **3e**–**g** with hydrazine monohydrate in DME by refluxing to prepare **4a**–**c** (Scheme 2, Table 2), and confirmed the stereochemistry of compound **4a** by X-ray diffraction analysis (Fig. 1 [11]). This fact led to a mechanism for the stereoselective formation of cyclopropane ring fused pyridazinone derivatives outlined in Scheme 3. The hydrazone **A** was formed by the condensation of carbonyl group on the cyclopropane **3** with hydrazine, and then the intramolecular nucleophilic addition–elimination between the ester group and the free amino group of hydrazone generated **4**. Thus, to form **4a**, PhCO and CO_2Me in **3e** would only be cis, which at last established the trans relationship of the *p*-trifluoromethylphenyl and PhCO groups. Therefore, we found a facile method to synthesize *trans*-1,2-cyclopropanes **3**. Additionally, this method provides a quick and efficient entry to functionalized pyrazole derivatives of biological interest due to the well known fact that the reactivity of the cyclopropanes with carbonyl group is similar to that of α,β-unsaturated carbonyl compounds.[12] 1,2-*trans*-Cyclopropanes **3b**–**d** reacted with hydrazine monohydrate by refluxing in DME to afford 3-aryl-5-*p*-trifluoromethylphenylpyrazoles **5a**–**c** in good to excellent yields (Scheme 2, Table 2). The structure of **5a** was confirmed by its X-ray diffraction analysis (Fig. 2 [11]). The mechanism was also proposed as shown in Scheme 4. In this reaction, the first step was the



Scheme 2.

Table 2
Preparation of pyrazole and pyridazinone derivatives

Entry	3	R_1	R_3	Product	Yield[a] (%)
1	**3e**	–C(O)Ph	–Ph	**4a**	88
2	**3f**	–C(O)(furan-2-yl)	–(Furan-2-yl)	**4b**	82
3	**3g**	–C(O)(thiophen-2-yl)	–(Thiophen-2-yl)	**4c**	74
4	**3b**	–C(O)Ph	–Ph	**5a**	90
5	**3c**	–C(O)(furan-2-yl)	–(Furan-2-yl)	**5b**	80
6	**3d**	–C(O)(thiophen-2-yl)	–(Thiophen-2-yl)	**5c**	78

[a] Isolated yield.

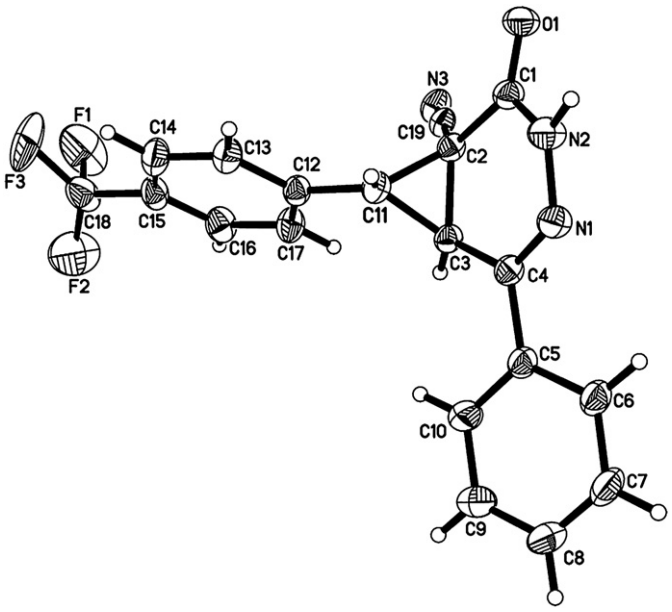


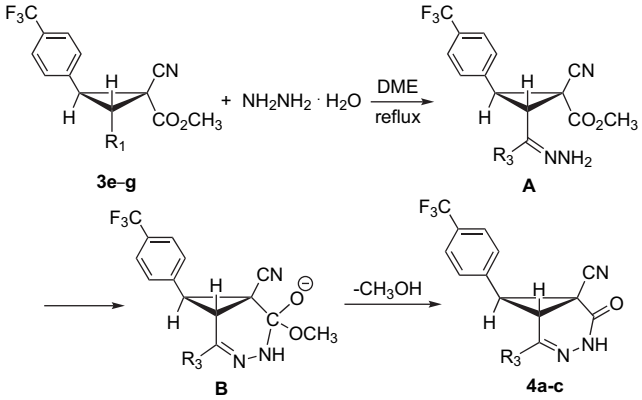
Figure 1. X-ray structure of compound **4a**.

condensation of carbonyl group on the cyclopropane with hydrazine providing hydrazone **C**. The intramolecular nucleophilic addition between the cyclopropane ring and the free amino group of hydrazone was involved in the second step to generate the pyrazoline **D**, followed by the easy transformation of pyrazoline **D** into pyrazoline **E**. The aromatization of pyrazoline **E** to pyrazoline **F** in the last step was achieved by the elimination of malononitrile in the presence of hydrazine as the base.

The packing diagrams of compounds **4a** (Fig. 3 [11]) and **5a** (Fig. 4 [11]) showed that there were intermolecular hydrogen bonds existing in each molecule with bond lengths of 3.037 Å and 2.905 Å, respectively. It also showed π–π stacking in compound **5a** with molecular layer distance of 3.5923 Å, which indicated the good coplanar feature of compound **5a**.

3. Conclusions

In summary, highly functionalized 1,2-*trans*-cyclopropanes containing trifluoromethyl group were stereoselectively synthesized under mild conditions in good yields. These versatile cyclopropane building blocks were successfully applied to the synthesis of pyrazole and cyclopropane ring fused pyridazinone derivatives.



Scheme 3.

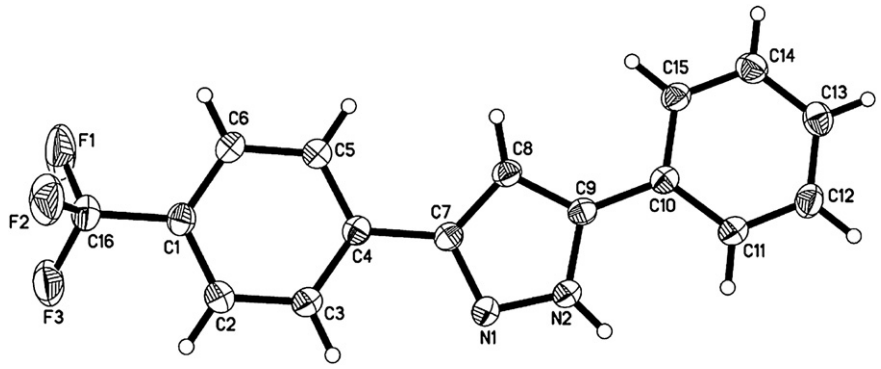
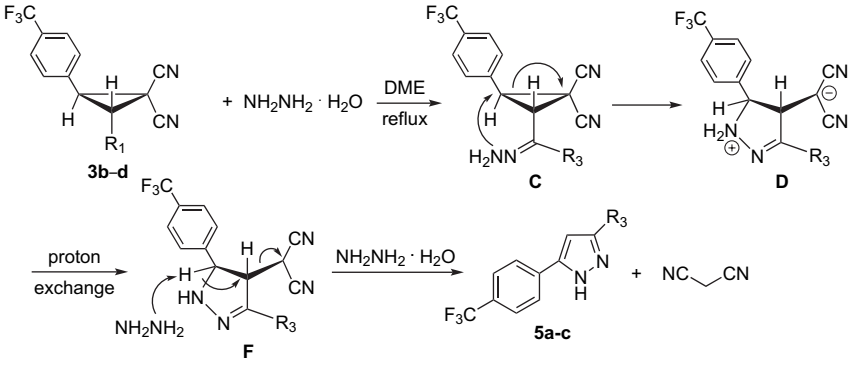


Figure 2. X-ray structure of compound **5a**.



Scheme 4.

4. Experimental

4.1. General information

All reagents and solvents were obtained from commercial sources and used without further purification. All melting points were uncorrected. Melting points were determined on a WRS-1 digital melting point apparatus made by Shanghai physical instrument factory (SPOIF), China. IR spectra were measured on

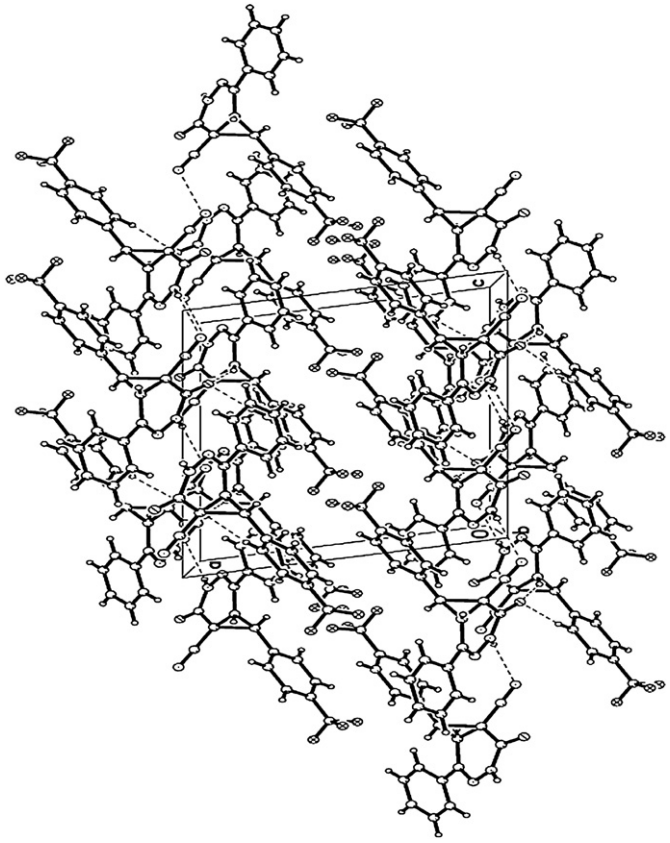


Figure 3. Packing diagram of compound **4a**.

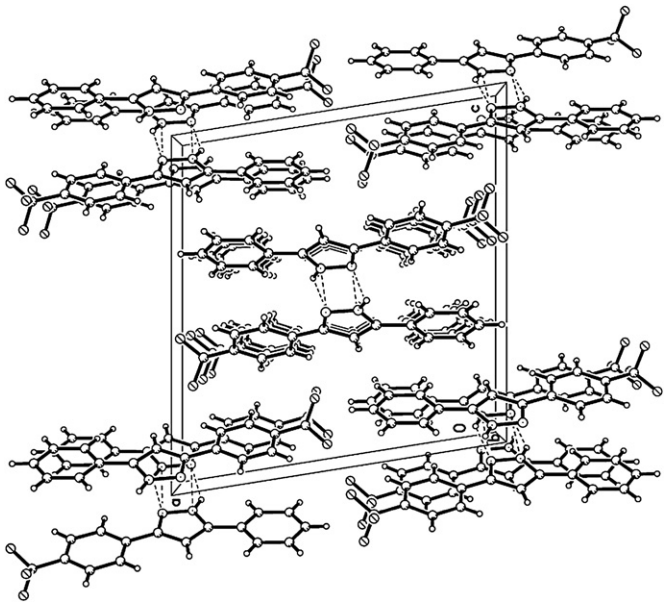


Figure 4. Packing diagram of compound **5a**.

a AVATAR370 FT spectrometer and expressed in cm^{-1} (KBr disc). All ^1H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker AM-500, using $CDCl_3$ as solvent. Mass spectra were recorded on an HP5989A mass spectrometer. HRMS spectra were run on a Waters Micromass GCT instrument. Elemental analyses were measured on the elementar vario EL III. X-ray crystal data were collected with a Bruker Smart Apex2 CCD. Flash chromatography was performed on columns of silica gel (20–30 μm).

4.2. General procedure for preparation of compound 3

Olefin **2** was prepared from malononitrile or methyl 2-cyanoacetate (1.1 mmol) and *p*-trifuoromethylbenzaldehyde (1.0 mmol) in methanol (5.0 mL) in the presence of piperidine (0.05 mL) followed by gentle heating at 50 °C until the aldehyde was consumed. A mixture of olefin **2** (1 mmol), arsonium salt **1** (1.2 mmol), and K_2CO_3 (3 mmol) was stirred at room temperature in $CHCl_3$ (5 mL). The completion of the reaction was monitored by TLC. The solid was filtered off and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel (eluent: petroleum ether 60–90 °C–ethyl acetate) to give the desired product **3**.

4.2.1. Compound *3a*

Yellow oil; ^1H NMR ($CDCl_3$) δ: 3.16 (d, J=8.0 Hz, 1H, CH), 3.76 (d, J=8.0 Hz, 1H, CH), 7.45–7.76 (m, 4H, ArH); ^{19}F NMR ($CDCl_3$) δ: −63.1 (s, CF_3); ^{13}C NMR ($CDCl_3$) δ: 135.2, 132.9 ($^2J_{C-F}$=32.7 Hz), 131.1, 126.8 ($^3J_{C-F}$=3.7 Hz), 124.2 ($^1J_{C-F}$=271.5 Hz), 112.5, 110.7, 109.5, 38.2, 20.1, 14.2; IR (film) ν: 2256, 1731, 843, 760, 734 cm^{-1}; MS m/z (EI): 261.0 (M^+); HRMS (EI): calcd for $C_{13}H_6N_3F_3$ (M^+) 261.0514, found 261.0520.

4.2.2. Compound *3b*

Yellow oil; ^1H NMR ($CDCl_3$) δ: 3.97 (d, J=8.0 Hz, 1H, CH), 4.10 (d, J=8.0 Hz, 1H, CH), 7.52–8.12 (m, 9H, ArH); ^{19}F NMR ($CDCl_3$) δ: −62.9 (s, CF_3); ^{13}C NMR ($CDCl_3$) δ: 188.4, 138.1, 135.4, 133.5, 132.0 ($^2J_{C-F}$=32.9 Hz), 139.5, 129.1, 129.0, 126.4 ($^3J_{C-F}$=3.6 Hz), 124.5 ($^1J_{C-F}$=271.0 Hz), 111.9, 111.2, 35.6, 32.2, 15.2; IR (film) ν: 2250, 1680, 846, 734, 708 cm^{-1}; MS m/z (EI): 340.0 (M^+); HRMS (EI): calcd for $C_{19}H_{11}ON_2F_3$ (M^+) 340.0823, found 340.0812.

4.2.3. Compound *3c*

Yellow oil; ^1H NMR ($CDCl_3$) δ: 3.91 (d, J=8.0 Hz, 1H, CH), 4.11 (d, J=8.0 Hz, 1H, CH), 6.75 (dd, J=1.0, 1.1 Hz, 1H, furan-H), 7.53–7.73 (m, 4H, ArH), 7.54 (d, J=1.1 Hz, 1H, furan-H), 7.80 (d, J=1.0 Hz, 1H, furan-H); ^{19}F NMR ($CDCl_3$) δ: −62.9 (s, CF_3); ^{13}C NMR ($CDCl_3$) δ: 176.6, 151.7, 148.7, 133.4, 131.0 ($^2J_{C-F}$=32.9 Hz), 126.3 ($^3J_{C-F}$=4 Hz), 125.0, 124.7, 124.5 ($^1J_{C-F}$=272.0 Hz), 114.0, 111.8, 111.0, 37.2, 35.2, 15.1; IR (film) ν: 2251, 1671, 847 cm^{-1}; MS m/z (EI): 331.1 [(M+1)]$^+$; HRMS (EI): calcd for $C_{17}H_{10}O_2N_2F_3$ [(M+H)]$^+$ 331.0694, found 331.0695.

4.2.4. Compound *3d*

Yellow oil; ^1H NMR ($CDCl_3$) δ: 3.95 (d, J=8.0 Hz, 1H, CH), 4.97 (d, J=8.0 Hz, 1H, CH), 7.30 (dd, J=4.0, 5.0 Hz, 1H, thiophene-H), 7.52–7.73 (m, 4H, ArH), 7.90 (d, J=5.0 Hz, 1H, thiophene-H), 8.05 (d, J=4.0 Hz, 1H, thiophene-H); ^{19}F NMR ($CDCl_3$) δ: −62.9 (s, CF_3); ^{13}C NMR ($CDCl_3$) δ: 180.4, 142.2, 137.5, 135.2, 134.4, 133.4, 132.0 ($^2J_{C-F}$=32.9 Hz), 129.0, 126.4 ($^3J_{C-F}$=3.6 Hz), 124.6 ($^1J_{C-F}$=270.2 Hz), 111.8, 111.1, 37.5, 36.3, 15.1; IR (film) ν: 2249, 1656, 850 cm^{-1}; MS m/z (EI): 347.0 (M^+); HRMS (EI): calcd for $C_{17}H_{10}ON_2F_3S$ [(M+H)]$^+$ 347.0466, found 347.0467.

4.2.5. Compound *3e*

Yellow oil; ^1H NMR ($CDCl_3$) δ: 3.73 (s, 3H, OCH_3), 3.74 (d, J=8.5 Hz, 1H, CH), 3.89 (d, J=8.5 Hz, 1H, CH), 7.52–8.02 (m, 9H, ArH); ^{19}F NMR ($CDCl_3$) δ: −62.72 (s, CF_3); ^{13}C NMR ($CDCl_3$) δ: 189.1, 164.0, 135.8, 135.2, 134.6, 131.2 ($^2J_{C-F}$=32.8 Hz), 129.2, 128.8, 128.5, 126.1 ($^3J_{C-F}$=3.8 Hz), 125.0, 124.0 ($^1J_{C-F}$=271.5 Hz), 114.9, 54.1, 34.6, 14.2; IR (film) ν: 2242, 1739, 1683, 1326 cm^{-1}; MS m/z (EI): 374.2 [(M+1)]$^+$; HRMS (EI): calcd for $C_{20}H_{14}O_3NF_3$ (M^+) 373.0926, found 373.0923.

4.2.6. Compound *3f*

Yellow oil; ^1H NMR ($CDCl_3$) δ: 3.71 (d, J=8.5 Hz, 1H, CH), 3.79 (s, 3H, OCH_3), 3.97 (d, J=8.5 Hz, 1H, CH), 6.63 (d, J=1.5 Hz, 1H, furan-H), 7.37 (d, J=3.5 Hz, 1H, furan-H), 7.52–7.68 (m, 4H, ArH), 7.70 (dd, J=1.5, 3.5 Hz, 1H, furan-H); ^{19}F NMR ($CDCl_3$) δ: −62.72 (s, CF_3); ^{13}C NMR ($CDCl_3$) δ: 177.9, 163.9, 151.8, 147.9, 135.9, 131.1 ($^2J_{C-F}$=32.8 Hz), 129.6, 128.9, 126.0 ($^3J_{C-F}$=3.8 Hz), 123.4 ($^1J_{C-F}$=271.5 Hz), 119.4, 113.2, 54.1, 28.6, 34.4, 14.2; IR (film) ν: 2247, 1746, 1676, 1326 cm^{-1}; MS m/z (EI): 364.2 [(M+1)]$^+$; HRMS (EI): calcd for $C_{18}H_{13}O_4NF_3$ [(M+H)]$^+$ 364.0797, found 364.0725.

4.2.7. Compound *3g*

Yellow oil; ^1H NMR ($CDCl_3$) δ: 3.67 (d, J=8.5 Hz, 1H, CH), 3.78 (s, 3H, OCH_3), 3.91 (d, J=8.5 Hz, 1H, CH), 7.21 (dd, J=3.0, 5.0 Hz, 1H, thiophene-H), 7.52–7.71 (m, 4H, ArH), 7.78 (d, J=5.0 Hz, 1H, thiophene-H), 7.85 (d, J=3.0 Hz, 1H, thiophene-H); ^{19}F NMR ($CDCl_3$) δ: −62.74 (s, CF_3); ^{13}C NMR ($CDCl_3$) δ: 181.6, 163.8, 142.2, 135.8, 131.2 ($^2J_{C-F}$=32.8 Hz), 129.5, 128.9, 128.8, 128.7, 126.1 ($^3J_{C-F}$=3.6 Hz), 124.0 ($^1J_{C-F}$=271.0 Hz), 114.8, 54.2, 39.9, 35.7, 14.2; IR (film) ν: 2247, 1746, 1666, 1326, 848 cm^{-1}; MS m/z (EI): 380.0 [(M+1)]$^+$; HRMS (EI): calcd for $C_{18}H_{13}O_3NF_3S$ [(M+H)]$^+$ 380.0568, found 380.0467.

4.2.8. Compound *3h*

Yellow oil; ^1H NMR ($CDCl_3$) δ: 3.65 (s, 3H, OCH_3), 3.73 (d, J=9.0 Hz, 1H, CH), 3.91 (d, J=9.0 Hz, 1H, CH), 7.36–7.70 (m, 9H, ArH); ^{19}F NMR ($CDCl_3$) δ: −62.67 (s, CF_3); ^{13}C NMR ($CDCl_3$) δ: 171.2, 167.9, 164.0, 130.5, 130.2 ($^2J_{C-F}$=32.8 Hz), 129.1, 128.9, 128.8, 125.9 ($^3J_{C-F}$=3.6 Hz), 124.9 ($^1J_{C-F}$=271.3 Hz), 116.2, 53.7, 40.8, 35.8, 14.2; IR (film) ν: 2243, 1742, 1325, 842, 759, 698 cm^{-1}; MS m/z (EI): 346.2 [(M+1)]$^+$; HRMS (EI): calcd for $C_{19}H_{14}O_2NF_3$ (M^+) 345.0977, found 345.0978.

4.3. General procedure for preparation of compound 4 or 5

The mixture of compound **3** (1.0 mmol) and hydrazine monohydrate (85%, 1.2 mmol) was refluxed in DME (5 mL) until TLC showed the completion of the reaction. After cooling, DME was removed in vacuo and the product was purified by flash chromatography on silica gel (eluent: petroleum ether 60–90 °C–ethyl acetate).

4.3.1. Compound *4a*

Yellow solid, mp: 217.6–218.9 °C; ^1H NMR ($CDCl_3$) δ: 3.15 (d, J=6.5 Hz, 1H, CH), 3.66 (d, J=7 Hz, 1H, CH), 7.46–7.76 (m, 9H, ArH), 9.16 (s, 1H, NH); ^{19}F NMR ($CDCl_3$) δ: −62.8 (s, CF_3); ^{13}C NMR ($CDCl_3$) δ: 131.7 ($^2J_{C-F}$=32.5 Hz), 131.1, 129.2, 128.6, 126.5 ($^3J_{C-F}$=3.7 Hz), 126.4, 123.8 ($^1J_{C-F}$=271.3 Hz), 115.1, 113.5, 32.1, 31.7, 29.8, 26.8, 22.8, 14.3; IR (film) ν: 3452, 3071, 2924, 2249, 1682, 1327, 1125, 845, 690 cm^{-1}; MS m/z (EI): 355.2 (M^+). Anal. Calcd for $C_{19}H_{12}O\,N_3F_3$: C, 64.23; H, 3.40; N, 11.83. Found: C, 64.20; H, 3.73; N, 11.19.

4.3.2. Compound *4b*

Yellow solid, mp: 199.2–202.2 °C; ^1H NMR ($CDCl_3$) δ: 3.14 (d, J=6.5 Hz, 1H, CH), 3.69 (d, J=6.5 Hz, 1H, CH), 6.59 (m, 1H, furan-H), 6.94 (d, J=3.5 Hz, 1H, furan-H), 7.62 (m, 1H, furan-H), 7.65 (m, 4H, ArH), 8.86 (s, 1H, NH); ^{19}F NMR ($CDCl_3$) δ: −62.8 (s, CF_3); ^{13}C NMR ($(CD_3)_2CO$) δ: 158.7, 150.4, 145.8, 137.8, 137.5, 130.9 ($^2J_{C-F}$=31.9 Hz), 130.2, 126.5 ($^3J_{C-F}$=3.4 Hz), 125.2 ($^1J_{C-F}$=270.0 Hz), 115.0, 113.0, 112.3, 32.2, 31.0, 27.6, 23.3, 14.4; IR (film) ν: 3456, 2923, 2854, 2251, 1670, 1132, 1069, 765 cm^{-1}; MS m/z (EI): 345.2 (M^+). Anal. Calcd for

$C_{17}H_{10}O_2N_3F_3$: C, 59.14; H, 2.92; N, 12.17. Found: C, 59.17; H, 3.08; N, 11.88.

4.3.3. Compound **4c**

Yellow solid, mp: 218.8–220.1 °C; ^{1}H NMR ($CDCl_3$) δ: 3.16 (d, J=6.5 Hz, 1H, CH), 3.65 (d, J=6.5 Hz, 1H, CH), 7.13 (m, 1H, thiophene-H), 7.42 (m, 1H, thiophene-H), 7.50 (m, 1H, thiophene-H), 7.65 (m, 4H, ArH), 8.63 (m, 1H, NH); ^{19}F NMR ($CDCl_3$) δ: −66.1 (s, CF_3); ^{13}C NMR ((CD_3)$_2$CO) δ: 158.8, 141.6, 140.7, 137.8, 130.9 ($^2J_{C-F}$=31.8 Hz), 130.2, 130.0, 129.4, 128.7, 126.5 ($^3J_{C-F}$=3.8 Hz), 125.2 ($^1J_{C-F}$=270 Hz), 115.0, 32.5, 31.4, 27.9, 23.3, 14.1; IR (film) ν: 3443, 2923, 2853, 2249, 1679, 1326, 1123, 845, 710 cm^{-1}; MS m/z (EI): 361.1 (M^+). Anal. Calcd for $C_{17}H_{10}ON_3F_3S$: C, 56.51; H, 2.79; N, 11.63. Found: C, 56.48; H, 2.92; N, 11.55.

4.3.4. Compound **5a**

White solid, mp: 142–144 °C; ^{1}H NMR ($CDCl_3$) δ: 6.91 (s, 1H, CH), 7.40–7.90 (m, 9H, Ph–H); ^{19}F NMR ($CDCl_3$) δ: −62.53 (s, CF_3); IR (film) ν: 3140, 760, 680 cm^{-1}; MS m/z (EI): 288.0 (M^+). Anal. Calcd for $C_{16}H_{11}N_2F_3$: C, 66.66; H, 3.85; N, 9.72. Found: C, 66.28; H, 4.06; N, 9.32.

4.3.5. Compound **5b**

White solid, mp: 152–154 °C; ^{1}H NMR ($CDCl_3$) δ: 6.52 (m, 1H, J=1.5, 3.0 Hz, furan-H), 6.68 (d, 1H, J=3.0 Hz, furan-H), 6.83 (s, 1H, CH), 7.49 (d, 1H, J=1.5 Hz, furan-H), 7.68–7.90 (m, 4H, ArH); ^{19}F NMR ($CDCl_3$) δ: −62.55 (s, CF_3); IR (film) ν: 3205, 751, 687 cm^{-1}; MS m/z (EI): 278.0 (M^+). Anal. Calcd for $C_{14}H_9ON_2F_3$: C, 60.44; H, 3.26; N, 10.07. Found: C, 60.28; H, 3.47; N, 9.65.

4.3.6. Compound **5c**

White solid, mp: 168–169 °C; ^{1}H NMR ($CDCl_3$) δ: 6.82 (s, 1H, CH), 7.11 (m, 1H, thiophene-H), 7.34 (m, 2H, thiophene-H), 7.69–7.85 (m, 4H, ArH); ^{19}F NMR ($CDCl_3$) δ: −62.58 (s, CF_3); IR (film) ν: 3158, 829, 757 cm^{-1}; MS m/z (EI): 294.0 (M^+). Anal. Calcd for $C_{14}H_9N_2F_3S$: C, 57.14; H, 3.08; N, 9.52. Found: C, 57.35; H, 3.42; N, 9.34.

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11. CCDC-651125 (**4a**) and CCDC-651124 (**5a**) contain all crystallographic details of this publication and are available free of charge at www.ccdc.cam.ac.uk/consts/retrieving.html or can be ordered from the following address: Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB21EZ; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk. Unit cell parameters (**4a**): a=11.5304 Å, b=11.3696 Å, c=13.3334 Å; β=100.007; space group: $P2(1)/c'$. Unit cell parameters (**5a**): a=14.7249 Å, b=5.8139 Å, c=15.6286 Å; β=99.054; space group: $P2(1)/n'$.
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