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N-Arylation of 4-fluoro-5-trimethylsilyl-1*H*-pyrazole

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Abstract

The 1,3-dipolar cycloaddition reaction of fluoro(trimethylsilyl)acetylene prepared *in situ* with an excess of diazomethane smoothly proceeded to give the corresponding 4-fluoro-5-trimethylsilyl-1*H*-pyrazole in 84% yield. The copper iodide-catalyzed *N*-arylation of the fluorinated pyrazole with a variety of aryl iodides afforded *N*-aryl-4-fluoropyrazoles as desilylation products in good to excellent yields.

Keywords: 4-Fluoro-5-trimethylsilyl-1*H*-pyrazole; *N*-Aryl-4-fluoropyrazole; *N*-Arylation; Copper catalyst; Fluoro(trimethylsilyl)acetylene

1. Introduction

N-Arylpyrazole structures are often encountered in pharmaceuticals and agrochemicals [1]. Much effort has been made to construct such an *N*-arylpyrazole structural unit. A general method for its preparation consists of condensation of *N*-arylhydrazines with a variety of 1,3-carbonyl compounds or its related compounds [2–7]. On the other hand, an alternative method has recently been developed by the transition metal-catalyzed *N*-arylation of 1*H*-pyrazoles [8–14]. We have previously reported a convenient method for the preparation of 5-tributylstannyl-4-fluoro-1*H*-pyrazole and its palladium-catalyzed cross-coupling reaction with various aryl iodides [15]. As an extension of this study, we became interested in the *N*-arylation of 5-tributylstannyl-4-fluoro-1*H*-pyrazole. For the sake of achievement of this reaction, the copper iodide-catalyzed *N*-arylation method appears the promising way due to high efficiency, easy procedure and reagent availability. Attempts to perform the *N*-arylation of the stannylpyrazole under these reaction conditions employed for pyrazole resulted in decomposition of the stannylpyrazole. To overcome this problem, we paid our attention to the reactivity and stability of the corresponding silylpyrazole. In this article, we report the preparation of 4-fluoro-5-trimethylsilyl-1*H*-pyrazole and its copper iodide-catalyzed *N*-arylation with various aryl iodides.

2. Results and discussion

According to our previous method for the preparation of 5-tributylstannyl-4-fluoro-1*H*-pyrazole from 1,1-difluoroethylene [15], 4-fluoro-5-trimethylsilyl-1*H*-pyrazole (**3**) was also prepared in 84% yield (Scheme 1). This method consists of the synthesis of fluoro(trimethylsilyl)acetylene (**2**) *in situ* and its successive 1,3-dipolar cycloaddition reaction with diazomethane. Attempts to isolate **2** invariably resulted in decomposition probably due to its thermal instability. It is noteworthy that no regioisomer was detected by GC–MS analysis in the crude reaction mixture. The fluorinated pyrazole (**3**) thus produced was a stable white solid and can be stored at room temperature at least for 6 months without deterioration.

The regiochemistry of the cycloaddition was next determined. After **3** was transformed into the corresponding desilylation pyrazole (**4**) by using of TBAF, the structural assignment was performed on the basis of the comparison of the corresponding ^{19}F NMR chemical shift value in the literature [15] (Scheme 2). The fluorine signal of **4** appeared at δ −181.3 ppm in the ^{19}F NMR in comparison with the reported value (−180.8 ppm), which revealed that the assigned pyrazole structure had the correct regiochemistry.

We carried out the DFT calculations using Spartan '04 at the B3LYP/6-31G* level of theory to support the observed regioselectivity in terms of HOMO–LUMO interaction as discussed in the literature [16,17]. The HOMO coefficient of diazomethane and the LUMO coefficient of fluoro(trimethylsilyl)acetylene (**2**) should support favor bond forming orientation in this 1,3-dipolar cycloaddition reaction (Table 1).

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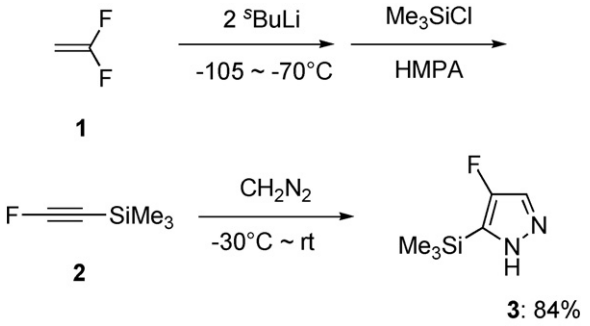
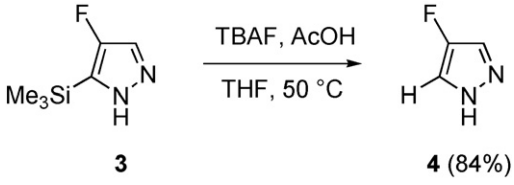


Scheme 1. One-pot synthesis of **3**.



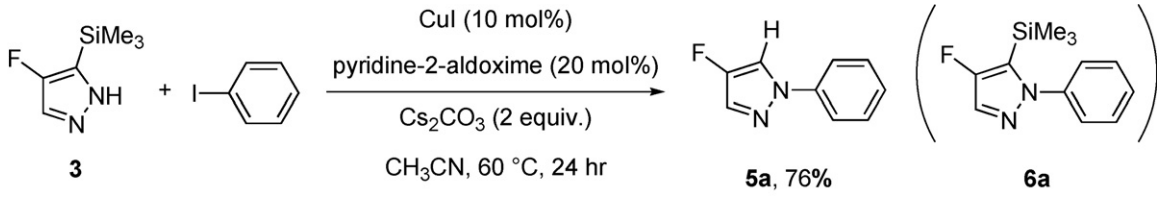
Scheme 2. Desilylation of **3**.

As mentioned above, several methods concerning the copper iodide-catalyzed *N*-arylation of various pyrazoles have been reported [8–14]. Among them, Cristau's report prompted us to apply their method to the preparation of *N*-aryl-4-fluoro-5-trimethylsilyl-1*H*-pyrazole [11]. When **3** (1 equiv.) was reacted with iodobenzene (1.1 equiv.) under the almost original standard conditions [CuI (10 mol%), pyridine-2-aldoxime (20 mol%) and Cs_2CO_3 (2 equiv.) in CH_3CN at 60 °C for 24 h], *N*-aryl-4-fluoro-pyrazole (**5a**) as the desilylation product was produced in 76% yield (Scheme 3). The desired *N*-aryl-4-fluoro-5-trimethylsilyl-1*H*-pyrazole (**6a**) was not observed at all. We monitored the reaction process by GC–MS analysis and found that the desilylation of **3** was initially and completely occurred and then *N*-arylation of the resulting 4-fluoropyrazole proceeded under these reaction conditions. No *N*-aryl-4-fluoro-5-trimethylsilyl-1*H*-pyrazole was detected during the reaction by GC–MS analysis.

Table 1
DFT calculations of HOMO and LUMO coefficients for diazomethane and fluoro(trimethylsilyl)acetylene (**2**)

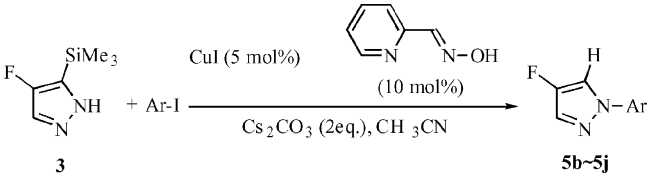
	CH_2N_2			$Me_3Si—≡—F$ (C1 C2)	
	HOMO	LUMO + 1		HOMO	LUMO
N	0.5366	0.6168	C1(Si)	0.1300	0.1854
C	−0.5965	0.6264	C2(F)	0.6314	−0.6408

Although a few synthetic routes to *N*-aryl-4-fluoropyrazoles have been reported [18–20], no *N*-arylation of 4-fluoropyrazole was examined. The generality of this *N*-arylation reaction was then demonstrated by the synthesis of other *N*-aryl-4-fluoropyrazoles (**5b**–**5j**). Theses results are summarized in Table 2. Although aryl iodides bearing an electron-withdrawing group were more suitable for the reaction to give the *N*-aryl-4-fluoropyrazoles in high to excellent yields, an aryl iodide bearing one electron-donating group at an ortho position required longer reaction time at a slightly higher temperature



Scheme 3. Copper(I)-catalyzed *N*-arylation of **3** with iodobenzene.

Table 2
N-Arylation of **3** with various aryl iodides[a]



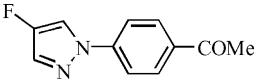
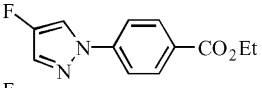
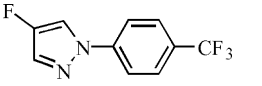
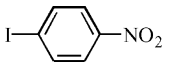
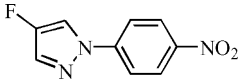
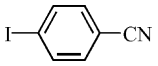
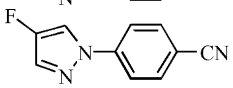
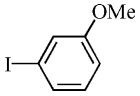
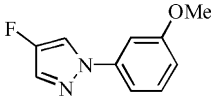
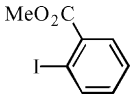
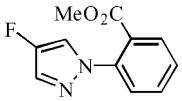
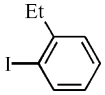
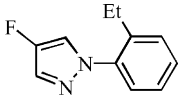
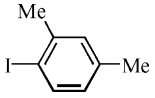
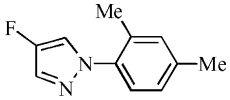
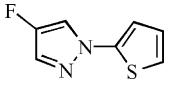
Entry	Arl	Time[b] (h)	Temperature (°C)	Product		Yield[c] (%)
1	I—C6H4—COMe	24	60		**5b**	82
2	I—C6H4—CO2Et	24	60		**5c**	76
3	I—C6H4—CF3	24	60		**5d**	86

Table 2 (*Continued*)

Entry	Arl	Time[b] (h)	Temperature (°C)	Product		Yield[c] (%)
4		24	60		**5e**	98
5		24	60		**5f**	98
6		24	60		**5g**	67
7		24	60		**5h**	89
8		144	70		**5i**	69
9		144	70		–	Trace
10		144	70		**5j**	46

[a] All reactions were conducted using **3** (1 equiv.) with aryl iodides (1.1–1.3 equiv.) in the presence of CuI (5 mol%), pyridine-2-aldoxime (10 mol%), and Cs_2CO_3 (2 equiv.) in CH_3CN.

[b] All reactions were monitored by GC–MS.

[c] Isolated yield.

(entry 8). Furthermore, no *N*-arylation occurred in the case of an aryl iodide bearing two electron-donating groups (entry 9). The substitution patterns on the aromatic ring seemed to have little influence on the product yield. The functional group compatibility (ketone, ester, ether, nitro) of the coupling reaction is noteworthy. Finally, a relevant heteroaromatic iodide was also effective for the *N*-arylation partner, albeit moderate yield (entry 10).

3. Conclusion

We have demonstrated the facile one-pot and high yield synthesis of 4-fluoro-5-trimethylsilyl-1*H*-pyrazole (**3**) via 1,3-dipolar cycloaddition reaction of fluoro(trimethylsilyl)acetylene (**2**) with diazomethane. The regiochemistry of the cycloaddition was confirmed by chemical transformation of the adduct and was also supported by the DFT calculations. The copper iodide-catalyzed *N*-arylation of **3** with a variety of aryl iodides smoothly proceeded to give the *N*-aryl-4-fluoropyrazoles in high yields. As far as this copper iodide-catalyzed *N*-arylation, **3** would be considered as the synthetic equivalent of 4-fluoropyrazole.

4. Experimental

Melting points are uncorrected. Infrared (IR) spectra are reported in cm^{-1}. ^1H, ^{19}F and ^{13}C NMR spectra were measured in $CDCl_3$ solutions. Chemical shifts were given by δ relative to that of an internal Me_4Si (TMS) for ^1H NMR and ^{13}C NMR spectra and benzotrifluoride ($CF_3C_6H_5$) for ^{19}F NMR spectra.

4.1. 4-Fluoro-5-trimethylsilyl-1H-pyrazole (3)

A 100 mL two-neck flask equipped with a magnetic stir bar, a stopcock and a three-way stopcock, was charged with 12.5 mL of THF under argon. To the stirred mixture was added *sec*-BuLi (1.0 M in cyclohexane solution, 9.0 mL, 9.0 mmol) dropwise via syringe at −78 °C. After this mixture had been stirred for an additional 10 min, the solution was cooled to −105 °C in a liquid N_2/ethanol bath. At this temperature, argon was replaced with 1,1-difluoroethylene (balloon). The mixture was gradually warmed to −70 °C. HMPA (0.15 mL) and chlorotrimethylsilane (Me_3SiCl, 0.52 mL, 4.07 mmol) were successively added dropwise to the solution by syringe. After the addition had been completed, the reaction mixture was allowed to warm to −30 °C. To the resulting reaction mixture was added an excess of ethereal diazomethane solution and the mixture was gradually warmed to room temperature. After hexane (10 mL) and water (20 mL) were successively added to the solution, the organic layer was separated from the mixture. The resulting aqueous layer was extracted with hexane/ether = 3/1 three times. After the combined organic layer was dried over sodium sulfate, and filtered through a short silica gel column (ether as an eluent), the eluate was concentrated in vacuo. The resulting oily residue was purified by silica gel column chromatography (hexane/ethyl acetate/triethylamine = 150/50/1) to give the desired product (**3**) as a white

solid (542.5 mg, 84%): mp 62.8–64.0 °C; IR (KBr) 3170, 3103, 2956, 1503, 1351, 1257, 1085, 954, 846 cm^{-1}; ^1H NMR ($CDCl_3$) 0.38 (9H, s), 7.46 (1H, d, J = 4.6 Hz), 9.85 (1H, brs); ^{19}F NMR ($CDCl_3$) −175.4 (1F, d, J = 3.6 Hz); ^{13}C NMR ($CDCl_3$) −1.63, 125.7 (d, J = 18.1 Hz), 127.3 (d, J = 34.3 Hz), 156.9 (d, J = 242.9 Hz); GC–MS *m/z* 158 (14, M^+), 143 (100), 142 (28), 89 (21), 88 (48), 81 (43), 77 (27), 73 (27), 63 (34), 54 (25); Anal. Calcd. for $C_6H_{11}FN_2Si$: C, 45.54; H, 7.01; N, 17.70. Found: C, 45.20; H, 6.85; N, 17.55%.

4.2. 4-Fluoro-1-phenylpyrazole (**5a**)

To a solution containing CuI (6.8 mg, 0.0375 mmol) and 2-pyridine-aldoxime (8.7 mg, 0.0712 mmol) in CH_3CN (1.5 mL) was successively added the pyrazole **1** (56.5 mg, 0.375 mmol), Cs_2CO_3 (233.5 mg, 0.717 mmol) and iodobenzene (47.9 μL, 0.428 mmol). The reaction mixture was heated to 60 °C, and stirred for 24 h. The reaction mixture was cooled to room temperature and diluted with hexane/ethyl acetate = 3/1. After filtration of a mixture through a plug of celite, the filter cake being further washed with hexane/ethyl acetate = 3/1. The combined filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ethyl acetate/triethylamine = 180/20/1 then 150/50/1) to give the desired compound (**5a**) as a white solid (43.7 mg, 76%): mp 37.5–38.2 °C; IR (KBr) 3130, 3108, 1599, 1582, 1505, 1411, 1370, 1016, 944, 839, 752, 688 cm^{-1}; ^1H NMR ($CDCl_3$) 7.25–7.33 (1H, m), 7.40–7.50 (2H, m), 7.57 (1H, d, J = 4.2 Hz), 7.60 (1H, q, J = 1.1 Hz), 7.63 (1H, q, J = 1.1 Hz), 7.80 (1H, dd, J = 4.8, 0.7 Hz); ^{19}F NMR ($CDCl_3$) −175.9 (1F, d, J = 4.8 Hz); ^{13}C NMR ($CDCl_3$) 112.9 (d, J = 28.0 Hz), 118.7, 126.7, 128.5 (d, J = 13.7 Hz), 129.5, 140.1, 151.2 (d, J = 248.5 Hz); GC–MS *m/z* 162 (62, M^+), 161 (27, $M^+ - 1$), 136 (16), 108 (71), 107 (47), 77 (100), 51 (59); Anal. Calcd. for $C_9H_7FN_2$: C, 66.66; H, 4.35; N, 17.27. Found: C, 66.75; H, 4.31; N, 17.30%.

4.3. 1-(4′-Acetylphenyl)-4-fluoropyrazole (**5b**)

White solid; yield 82%; mp 133.4–134.6 °C; IR (KBr) 3113, 1680, 1599, 1414, 1275, 1188, 1114, 1020, 947, 844, 831 cm^{-1}; ^1H NMR ($CDCl_3$) 2.63 (3H, s), 7.63 (1H, d, J = 4.2 Hz), 7.73 (2H, brd, J = 8.8 Hz), 7.89 (1H, d, J = 4.8 Hz), 8.06 (2H, brd, J = 8.8 Hz); ^{19}F NMR ($CDCl_3$) −174.9 (1F, d, J = 4.3 Hz); ^{13}C NMR ($CDCl_3$) 26.5, 112.9 (d, J = 28.6 Hz), 117.9, 129.8 (d, J = 14.3 Hz), 130.0, 135.1, 143.2, 151.5 (d, J = 251.0 Hz), 196.4; GC–MS *m/z* 204 (33, M^+), 189 (100), 188 (20), 161 (19), 134 (76), 133 (27), 107 (75), 76 (48), 63 (48), 50 (53); Anal. Calcd. for $C_{11}H_9FN_2O$: C, 64.70; H, 4.44; N, 13.72. Found: C, 64.69; H, 4.32; N, 13.82%.

4.4. 1-(4′-Ethoxycarbonylphenyl)-4-fluoropyrazole (**5c**)

White solid; yield 76%; mp 95.2–96.2 °C; IR (KBr) 3124, 2982, 1707, 1614, 1583, 1413, 1282, 1110, 1021, 942, 854, 769 cm^{-1}; ^1H NMR ($CDCl_3$) 1.41 (3H, t, J = 7.2 Hz), 4.40 (2H, q, J = 7.2 Hz), 7.62 (1H, d, J = 4.2 Hz), 7.70 (2H, dt, J = 8.8, 2.0 Hz), 7.88 (1H, dd, J = 4.8, 0.6 Hz), 8.13 (2H, dt, J = 8.8, 2.0 Hz); ^{19}F NMR ($CDCl_3$) −174.9 (1F, t, J = 4.1 Hz); ^{13}C NMR ($CDCl_3$) 14.3, 61.2, 112.9 (d, J = 28.0 Hz), 117.7, 128.5, 129.5 (d, J = 13.7 Hz), 131.1, 143.1, 151.3 (d, J = 250.4 Hz), 165.7; GC–MS *m/z* 234 (34, M^+), 189 (100), 161 (15), 134 (56), 107 (63), 76 (37), 50 (32); Anal. Calcd. for $C_{12}H_{11}FN_2O_2$: C, 61.53; H, 4.73; N, 11.96. Found: C, 61.48; H, 4.79; N, 11.94%.

4.5. 4-Fluoro-1-(4′-trifluoromethylphenyl)pyrazole (**5d**)

White solid; yield 86%; mp 60.2–61.1 °C; IR (KBr) 3145, 3085, 1621, 1606, 1529, 1410, 1328, 1168, 1134, 1070, 1019, 942, 856, 831, 779, 716 cm^{-1}; ^1H NMR ($CDCl_3$) 7.62 (1H, d, J = 4.2 Hz), 7.71 (2H, brd, J = 9.0 Hz), 7.76 (2H, brd, J = 9.0 Hz), 7.86 (1H, d, J = 4.8 Hz); ^{19}F NMR ($CDCl_3$) −64.4 (3F, s), −174.5 (1F, t, J = 4.8 Hz); ^{13}C NMR ($CDCl_3$) 112.9 (d, J = 28.6 Hz), 118.3, 122.1, 123.9 (q, J = 271.5 Hz), 126.8 (d, J = 3.7 Hz), 128.6 (q, J = 33.0 Hz), 129.7 (d, J = 13.7 Hz), 142.0, 151.5 (d, J = 251.0 Hz); GC–MS *m/z* 230 (90, M^+), 145 (100), 134 (39), 125 (45), 107 (37), 95 (73), 75 (65), 69 (21), 50 (28); Anal. Calcd. for $C_{10}H_6F_4N_2$: C, 52.18; H, 2.63; N, 12.17. Found: C, 52.33; H, 2.71; N, 12.14%.

4.6. 4-Fluoro-1-(4′-nitrophenyl)pyrazole (**5e**)

White solid; yield 98%; mp 144.3–145.0 °C; IR (KBr) 3143, 1593, 1525, 1409, 1336, 1180, 1112, 1017, 937, 847, 750 cm^{-1}; ^1H NMR ($CDCl_3$) 7.67 (1H, d, J = 4.2 Hz), 7.82 (2H, dt, J = 9.4, 2.8 Hz), 7.92 (1H, dd, J = 4.7, 0.7 Hz), 8.34 (2H, dt, J = 9.4, 2.8 Hz); ^{19}F NMR ($CDCl_3$) −172.9 (1F, t, J = 4.2 Hz); ^{13}C NMR ($CDCl_3$) 113.0 (d, J = 28.6 Hz), 118.13, 118.14, 125.4, 130.8 (d, J = 13.7 Hz), 144.2, 145.7, 151.8 (d, J = 252.9 Hz); GC–MS *m/z* 207 (38, M^+), 134 (67), 108 (20), 107 (100), 76 (54), 75 (56), 63 (60), 50 (64); Anal. Calcd. for $C_9H_6FN_3O_2$: C, 52.18; H, 2.92; N, 20.28. Found: C, 52.31; H, 2.88; N, 20.28%.

4.7. 1-(4′-Cyanophenyl)-4-fluoropyrazole (**5f**)

White solid; yield 98%; mp 124.0–125.0 °C; IR (KBr) 3063, 2229, 1600, 1524, 1412, 1183, 1167, 1018, 939, 837, 779 cm^{-1}; ^1H NMR ($CDCl_3$) 7.65 (1H, d, J = 4.0 Hz), 7.76 (4H, s), 7.87 (1H, d, J = 5.0 Hz); ^{19}F NMR ($CDCl_3$) −173.7 (1F, t, J = 3.7 Hz); ^{13}C NMR ($CDCl_3$) 109.9, 112.8 (d, J = 28.6 Hz), 118.2, 118.4, 130.3 (d, J = 14.3 Hz), 133.6, 142.8, 151.6 (d, J = 251.6 Hz); GC–MS *m/z* 187 (23, M^+), 133 (36), 115 (13), 102 (100), 75 (38), 51 (22); Anal. Calcd. for $C_{10}H_6FN_3$: C, 64.17; H, 3.23; N, 22.45. Found: C, 64.11; H, 3.23; N, 22.45%.

4.8. 4-Fluoro-1-(3′-methoxylphenyl)pyrazole (**5g**)

White solid; yield 67%; mp 55.6–56.1 °C; IR (KBr) 3115, 3100, 1596, 1505, 1411, 1376, 1263, 1248, 1210, 1056, 1024, 957, 848, 766 cm^{-1}; ^1H NMR ($CDCl_3$) 3.86 (3H, s), 6.84 (1H, ddd, J = 8.1, 2.2, 0.9 Hz), 7.15 (1H, ddd, J = 8.1, 2.2, 0.9 Hz), 7.24 (1H, t, J = 2.2 Hz), 7.33 (1H, t, J = 8.1 Hz), 7.56 (1H, brd, J = 4.8 Hz), 7.78 (1H, dd, J = 4.8, 0.6 Hz); ^{19}F NMR ($CDCl_3$)

−175.4 (1F, t, J = 3.9 Hz); ^{13}C NMR ($CDCl_3$) 55.5, 104.7, 110.7, 112.6, 113.1 (d, J = 28.0 Hz), 128.4 (d, J = 13.7 Hz), 130.2, 141.3, 151.1 (d, J = 249.1 Hz), 160.6; GC–MS *m/z* 192 (84, M^+), 191 (44, $M^+ - 1$), 149 (23), 122 (57), 107 (52), 92 (78), 77 (100), 64 (80), 63 (99), 51 (41); Anal. Calcd. for $C_{10}H_9FN_2O$: C, 62.49; H, 4.72; N, 14.58. Found: C, 62.48; H, 4.78; N, 14.57%.

4.9. 4-Fluoro-1-(2′-methoxycarbonylphenyl)pyrazole (**5h**)

Colorless oil; yield 89%; IR (NaCl) 3131, 2953, 1732, 1586, 1506, 1458, 1409, 1305, 1283, 1127, 1013, 946, 763 cm^{-1}; ^{1}H NMR ($CDCl_3$) 3.76 (3H, s), 7.40–7.50 (2H, m), 7.55–7.65 (3H, m), 7.82 (1H, dd, J = 7.6, 1.2 Hz); ^{19}F NMR ($CDCl_3$) −177.2 (1F, t, J = 4.2 Hz); ^{13}C NMR ($CDCl_3$) 52.4, 116.0 (d, J = 28.0 Hz), 125.0, 127.5, 128.1, 128.5 (d, J = 13.7 Hz), 130.5, 132.0, 139.2, 150.6 (d, J = 247.9 Hz), 166.9; GC–MS *m/z* 220 (48, M^+), 189 (100), 162 (20), 134 (48), 107 (45), 90 (20), 77 (34), 76 (32), 63 (28), 50 (33); Anal. Calcd. for $C_{11}H_9FN_2O_2$: C, 60.00; H, 4.12; N, 12.72. Found: C, 60.12; H, 4.10; N, 12.69%.

4.10. 1-(2′-Ethylphenyl)-4-fluoropyrazole (**5i**)

Colorless oil; yield 69%; IR (NaCl) 3129, 2970, 2934, 2875, 1582, 1501, 1408, 1361, 1012, 829, 762, 669 cm^{-1}; ^{1}H NMR ($CDCl_3$) 1.11 (3H, t, J = 7.5 Hz), 2.58 (2H, q, J = 7.5 Hz), 7.25–7.29 (2H, m), 7.30–7.42 (2H, m), 7.48 (1H, d, J = 4.6 Hz), 7.56 (1H, d, J = 3.9 Hz); ^{19}F NMR ($CDCl_3$) −178.7 (1F, t, J = 4.4 Hz); ^{13}C NMR ($CDCl_3$) 14.9, 24.3, 116.8 (d, J = 27.4 Hz), 126.5, 126.6, 127.5 (d, J = 13.7 Hz), 129.1, 129.7, 150.0 (d, J = 247.9 Hz); GC–MS *m/z* 190 (43, M^+), 148 (74), 130 (21), 117 (65), 103 (34), 89 (26), 77 (100), 51 (50); Anal. Calcd. for $C_{11}H_{11}FN_2$: C, 69.46; H, 5.83; N, 14.73. Found: C, 69.74; H, 5.72; N, 14.89%.

4.11. 4-Fluoro-1-(thiophen-2-yl)pyrazole (**5j**)

White solid; yield 46%; mp 44.5–45.0 °C; IR (KBr) 3126, 3103, 3068, 1584, 1543, 1472, 1427, 1397, 1359, 1237, 1152, 1006, 916, 847, 829, 784 cm^{-1}; ^{1}H NMR ($CDCl_3$) 6.93 (1H, dd, J = 5.1, 3.9 Hz), 6.96 (1H, dd, J = 3.9, 1.7 Hz), 7.04 (1H, dd, J = 5.1, 1.7 Hz), 7.52 (1H, d, J = 4.0 Hz), 7.69 (1H, d, J = 4.8 Hz); ^{19}F NMR ($CDCl_3$) −175.6 (1F, t, J = 4.1 Hz); ^{13}C NMR ($CDCl_3$) 114.3 (d, J = 26.8 Hz), 120.5, 126.0, 128.6 (d, J = 14.3 Hz), 143.8, 150.8 (d, J = 249.8 Hz); GC–MS *m/z* 168 (100, M^+), 123 (28), 114 (86), 96 (64), 88 (27), 70 (80), 57 (33); Anal. Calcd. for $C_7H_5FN_2S$: C, 49.99; H, 3.00; N, 16.66. Found: C, 50.08; H, 2.97; N, 16.73%.

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