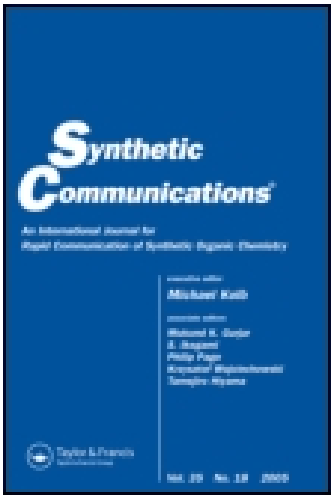

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Iron-Catalyzed Direct Sulfenylation and Selenylations of Phenylpyrazoles: Synthesis of Fipronil Derivatives with Disulfides Promoted by a Catalytic Amount of Iodine

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IRON-CATALYZED DIRECT SULFENYLATION AND SELENYLATIONS OF PHENYLPYRAZOLES: SYNTHESIS OF FIPRONIL DERIVATIVES WITH DISULFIDES PROMOTED BY A CATALYTIC AMOUNT OF IODINE

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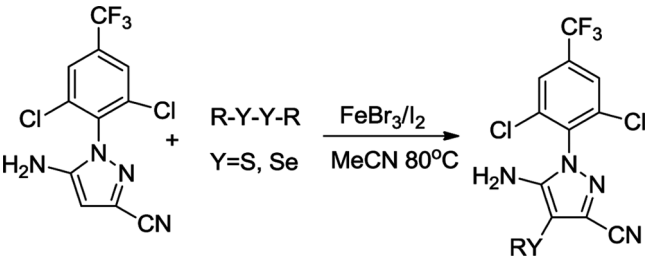
GRAPHICAL ABSTRACT



Abstract *The direct thiolation of phenylpyrazole with disulfide using the $FeBr_3/I_2$ complex as the catalyst in MeCN at 80 °C was reported. With the optimum conditions, several fipronil derivatives of 4-sulfenylpyrazole were synthesized by the reaction of 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl-lH-pyrazole-3-arbonitrile (**1a**) with disulfides (**2**) in moderate to good yields. The coupling reaction with diaryl diselane also occurred under similar conditions.*

Keywords Direct thiolation; $FeBr_3/I_2$-catalyzed system; fipronil derivatives; selenylpyrazole; sulfenylpyrazole

INTRODUCTION

N-Phenylpyrazole derivatives have attracted great attentions because of their biological activities.[1] For example, fipronil,[2] 5-amino-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethylsulfinyl-lH-pyrazole-3-carbonitrile (I, Fig. 1), is an important phenylpyrazole insecticide. Moreover, many fipronil analogs that have a thio group, such as fipronil sulfide (II),[3] sulfone (III),[4] and ethiprole (IV), with 4-EtSO replacing the 4-CF_3SO of (I) or ethiprole sulfide (V),[5] were also surprisingly

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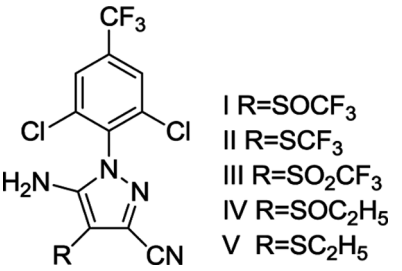
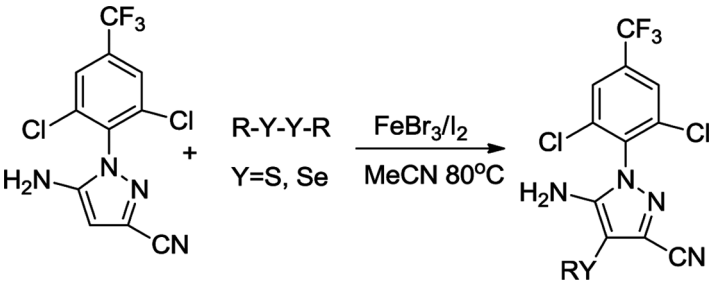


Figure 1. Fipronil (**I**) and analogs (**II, III, IV, V**).

found to have the same insecticidal activity. We believe that the fipronil derivatives of 4-sulfenylpyrazole, with 4-alkyl(aryl) thio replacing 4-CF_3SO of (I), may have the same high insecticidal activity.

The traditional synthesis of sulfenylpyrazole often used RSCl or ArSCl,[6] which are very toxic and difficult to prepare. Lin et al. and Lange et al.[7] have reported preparation of the 4-sulfenylpyrazole based on the reaction of 4-bromopyrazole with disulfide, which was undesirable from the viewpoint of atom economy. The synthesis of sulfenylpyrazole by other ways was reported rarely. In our group, we have been devoted to exploring different ways to introduce thio groups at the pyrazole moiety. For example, in 2006, we introduced alkylthio at the pyrazole ring by the reaction of 5-amino-1-(2,6-dichloro-4-trifluoromethylphenyl)-3-cyanopyrazolyldisulfied with alkyl halide in the presence of sodium dithionite at room temperature.[8] In 2008, alkenyl sulfides of pyrazole were synthesized by the reaction of disulfied with terminal alkynes in the presence of CuI, rongalite, and Cs_2CO_3.[9] Subsequently, a novel and solvent-free protocol for the synthesis of sulfenylpyrazole by the copper-catalyzed oxidative S-arylation of disulfides with aryltrimethoxysilanes was reported.[10] We also have sucessfully synthesized sulfenylpyrazole by the reaction of disulfiedes with organoboronic acids in the presence of copper catalysts.[11]

However, in view of these different methods, 5-amino-1-(2,6-dichloro-4-trifluoromethylphenyl)-3-cyanopyrazolyl disulfide must be synthesized based on the reaction of 5-amino-1-(2,6-dichloro-4-trifluoromethylphenyl)-3-cyanopyrazolyl (**1a**) with S_2Cl_2, which had a foul odor. We envisioned that sulfenylpyrazole could be



Scheme 1.

synthesized by the direct thiolation of pyrazole with disulfide, considering that the direct thiolation of hetercycles compounds is of current interest. Here, we report a protocol for the direct thiolation of phenylpyrazole with disulfide using the $FeBr_3$/I_2 complex as the catalyst in MeCN at 80 °C (Scheme 1). Moreover, the coupling reaction of pyrazole with diaryl diselane also occurred under similar conditions.

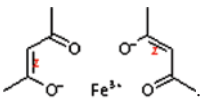
We started with the coupling reaction of 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl-lH-pyrazole-3-carbonitrile (**1a**) with 1,2-diphenyldisulfane (**2a**) to assess the catalyst activity and determine the optimal reaction conditions, and the results are summarized in Table 1. Initially, a series of Lewis acids, including FeF_3,

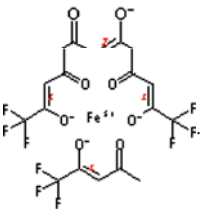
Table 1. Screening optimal conditions[a]

Entry	Fe (mol %)	Solvent Isolated yield[b] (%)
1	FeF_3 (10) MeCN	66
2	$FeCl_3$ (10) MeCN	76
3	$FeBr_3$ (10) MeCN	82
4	$Fe(C_5H_7O_2\ MeCN)_3$[c] (10)	20
5	$Fe(C_5H_7O_2\ MeCN\ F_3)_3$[d] (10)	75
6[e]	$FeBr_3$ (10) MeCN	0
7[f]	— MeCN	50
8	$FeBr_3$ (5) MeCN	70
9	$FeBr_3$ (20) MeCN	82
10[g]	$FeBr_3$ (10) MeCN	52
11[h]	$FeBr_3$ (10) MeCN	23
12	$FeBr_3$ (10) DCE	50
13	$FeBr_3$ (10) tolune	66
14	$FeBr_3$ (10) THF	23
15	$FeBr_3$ (10) DMF	Trace
16[i]	$FeBr_3$ (10) MeCN	81

[a]Reaction conditions: **1a** (0.4 mmol), **2a** (0.2 mmol), Fe (10 mol%), and I_2 (10 mol%) in solvent (3 mL) at 80 °C for 42 h.

[b]Isolated yield.

[c]The structure  .

[d]The structure  .

[e]Without I_2.

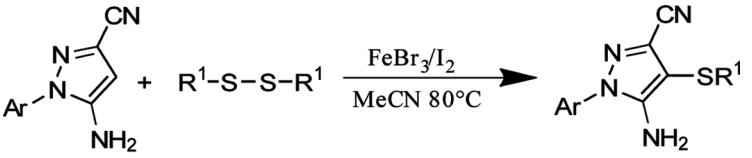
[f]I_2 (100 mol%).

[g]At 100 °C.

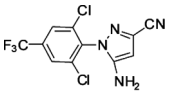
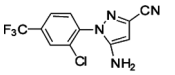
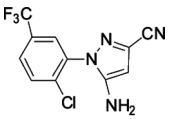
[h]At room temperature.

[i]Under N_2.

Table 2. Synthesis of 4-sulfenylated pyrazole by $FeBr_3/I_2$-catalyzed 4-sulfenylation of disulfides (**2b–2h**) with pyrazoles (**1a, 1b, 1c**)[a]



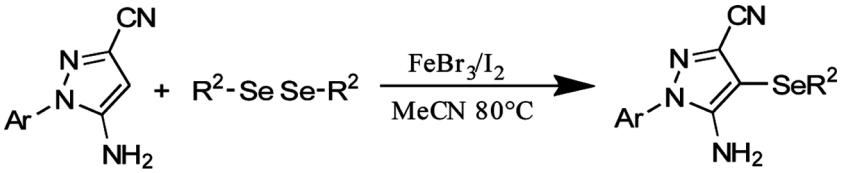
1a-1c 2b-2h 3

Entry	Pyrazole **1a–c**	R^1	Product	Yield (%)[b]
1	 **(1a)**	4-MeC_6H_4 (**2b**)	**3ab**[(11)]	92
2	(**1a**)	4-$MeOC_6H_4$ (**2c**)	**3ac**[(11)]	73
3	(**1a**)	4-ClC_6H_4 (**2d**)	**3ad**[(11)]	93
4	(**1a**)	4-FC_6H_4 (**2e**)	**3ae**[(11)]	95
5	(**1a**)	3-FC_6H_4 (**2f**)	**3af**	55
6	(**1a**)	4-$NO_2C_6H_4$ (**2 g**)		Trace
7	(**1a**)	Benzyl (**2 h**)	**3ah**[(11)]	90
8	 (**1b**)	(**2a**)	**3ba**	74
9	(**1b**)	(**2c**)	**3bc**	90
10	 **(1c)**	(**2a**)	**3ca**	75
11	(**1c**)	(**2c**)	**3cc**	64

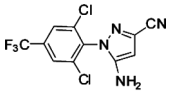
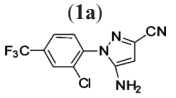
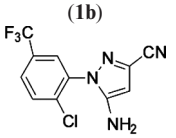
[a]Reaction conditions: **1** (0.4 mmol), **2** (0.2 mmol), $FeBr_3$ (10 mol%), and I_2 (10 mol%) in MeCN (3 mL) at 80 °C for 42 h.
[b]Isolated yield.

$FeCl_3$, $FeBr_3$, iron (III) 2, 4-pentanedionate [$Fe(C_5H_7O_2)_3$], and iron(III) trifluoro-pentanedirnat [$Fe(C_5H_7O_2F_3)_3$], were tested (entries 1–5). We found that the yield is 82% in the presence of $FeBr_3$ after 42 h at 80 °C (entry 3), and that the other Lewis acid catalysts were inferior to $FeBr_3$. Moreover, $FeBr_3$ was found to be less effective in the absence of iodine (entry 6), while 50% yield of product **3aa** was isolated using 100 mol% of iodine alone (entry 7). Among the amounts of $FeBr_3$ and the reaction temperatures examined, 20 mol% of $FeBr_3$ combined with 80 °C gave the same and the best yield (entry 7) with the 10 mol% of $FeBr_3$. A number of other solvents were also examined [dichloroethane (DCE), toluene, tetrahydrofuran (THF),

Table 3. Synthesis of 4-selenylated pyrazole by $FeBr_3/I_2$-catalyzed 4-selenylations of diselenides (**2i–2j**) with pyrazoles (**1a, 1b, 1c**)[a]

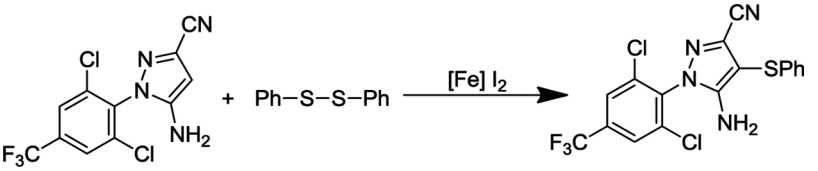


1a-1c 2i-2j 4

Entry	Pyrazole **1**	R^2	Product	Yield (%)[b]
1	 **(1a)**	Phenyl (**2i**)	**4ai**	46
2	(**1a**)	benzyl (**2j**)	**4aj**	78
3	 **(1b)**	(**2i**)	**4bi**	32
4	(**1b**)	(**2j**)	**4bj**	56
5	 **(1c)**	(**2i**)	**4ci**	55
6	(**1c**)	(**2j**)	**4cj**	53

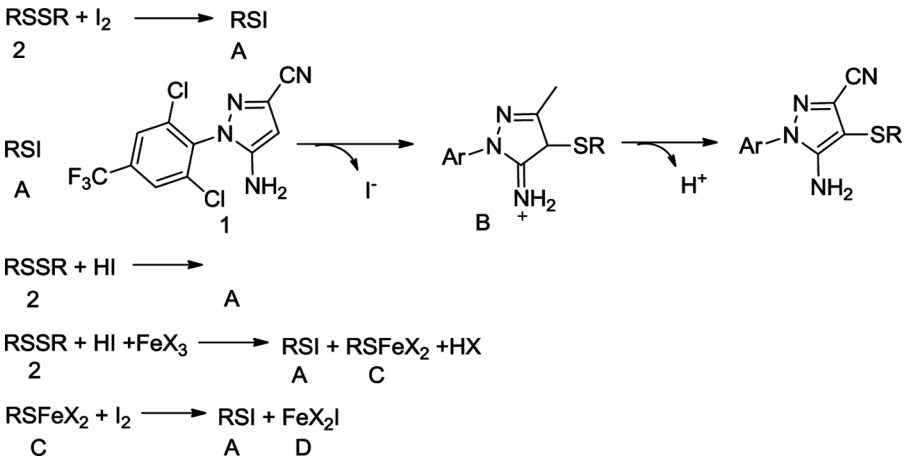
[a]Reaction conditions: **1** (0.4 mmol), **2i and j** (0.2 mmol), $FeBr_3$ (10 mol%), and I_2 (10 mol%) in MeCN (3 mL) at 80 °C for 42 h.

dimethylformamide (DMF); entries 12–15], and they were less effective than aceonitrile.



1a **2a** **3aa**

We then examined the scope with respect to phenylpyrazole **1a, 1b, 1c** and disulfides **2b–2h** under the optimized conditions; typical results are shown in Table 2. Initially, a variety of disulfides were examined with pyrazole (**1a**) (entries 1–7). The results demonstrated that diaryldisulfides **2b–2g**, bearing either electron-donating or electron-withdrawing groups, underwent direct thiolation of pyrazole (**1a**) (entries 1–5) smoothly, but the disulfide with nitro groups **2g** gave an unsatisfactory result (entries 6). To our delight, the reaction conditions are compatible with dialkyl disulfides 1; 2-dibenzyldisulfane (**2h**), for instance, underwent the reaction with pyrazole



Scheme 2. Working mechanism.

(**1a**), $FeBr_3$, and I_2 smoothly in 90% yield (entry 7). Subsequently, other substituted pyrazoles **1b** and **1c** were investigated (entries 8–11) under the standard conditions. It was noteworthy to discover that the reaction can give good yields.

The direct selenylation of pyrazoles with 1,2-diphenyl diselane and 1,2-dibenyldiselane were also tested under the standard conditions, and the results are summarized in Table 3. In the presence of $FeBr_3$ and I_2, pyrazoles **1a, 1b**, and **1c** underwent the 4-selenylation reaction with 1,2-diphenyl diselane and 1,2-dibenyl diselane smoothly to afford the corresponding 4-selenylated pyrazoles in moderate to good yields.

A possible working mechanism, as outlined in Scheme 2, was proposed on the basis of reported mechanisms.[12] The reaction can take place in the presence of iodine alone (Table 1, entry 6), which suggests an electrophilic addition process. Initially, intermediate RSI (**A**), which is afforded in situ by the reaction of RSSR (**2**) with I_2, undergoes the electrophilic addition to 5-amino-1-[2,6-dichloro-4-(trifluoromethyl) phenyl-lH-pyrazole-3-carbonitrile (**1**), leading to intermediate **B** with the aid of $FeBr_3$ catalyst. Deprotonation of intermediate **B** gives the desired product and HI. The reaction of HI with RSSR (**2**) may take place to provide the active intermediate RSI (**A**) and an inactive RSH intermediate.

In summary, we have developed a protocol for the synthesis of sulfenylated pyrazoles via iron-catalyzed direct thiolation of pyrazoles and disulfides with the aid of I_2. In comparison with the reported synthesis of sulfenylpyrazole, the present $FeBr_3/I_2$ system has advantages of good efficiency, simple operation, low cost, and security for regioselective sulfenylation of pyrazole. Moreover, the direct selenylation of pyrazoles with 1,2-diphenyldiselane and 1,2-dipbenyldiselane are also conducted efficiently to afford the corresponding 4-selenated pyrazoles in moderate to good yields using the $FeBr_3/I_2$ system.

EXPERIMENTAL

Chemicals were either purchased or purified by standard techniques. ^1H NMR and ^{13}C NMR spectra were measured on a 300-MHz spectrometer (^1H, 300 MHz;

^{13}C, 125 MHz), using $CDCl_3$ and actone-d_6 as the solvent with tetramethylsilane (TMS) as an internal standard at room temperature. The coupling constants J are given in hertz (Hz). The high-resolution mass spectrometer was a Waters Micromass GCT Premier (EI+, 70 eV). All reactions are happen under an air atmosphere. Column chromatography was performed using EM silica gel 60 (300–400 mesh).

Typical Experimental Procedure of the Iron-Catalyzed Sulfenylations of Pyrazoles (1) with Disulfides (2) in the Presence of I_2

A mixture of 5-amino-1-[2, 6-dichloro-4-(trifluoro methyl)-phenyl pyrazole-3-carbonitrile **1a** (0.2 mmol), 1,2-diphenyldisulfane **2a** (0.1 mmol), $FeBr_3$ (10 mol%), and I_2 (10 mol%) in MeCN (3 mL) was stirred at 80 °C for the indicated time until complete consumption of starting material as monitored by thin-layer chromatography (TLC). After the reaction was finished and cooled down, the mixture was poured into ethyl acetate, which was dried over anhydrous Mg_2SO_4, and evaporated under vacuum. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate) to afford the desired product.

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-(3-fluorophenyl) thio-1H-pyrazole-3-carbonitrile (3af)

White solid, mp 242–244 °C (uncorrected); ^1H NMR (500 MHz, acetone-d_6) δ: 7.27 (s, 2H), 6.65–6.50 (m, 1H), 6.18–6.02 (m, 3H), 5.52 (brs, 2H); ^{13}C NMR (125 MHz, actone-d_6) δ: 164.0 (d, $J = 245.2$ Hz), 153.3, 140.7, 137.3, 136.7, 134.8 (q, $J = 34.0$ Hz), 133.1, 131.8, 127.4, 123.3 (q, $J = 271.5$ Hz), 122.1, 113.3 (d, $J = 21.5$ Hz), 113.2, 112.8 (d, $J = 24.5$ Hz), 89.5; LRMS (EI, 70 eV) m/z (%): 446 (M^+, 100); HRMS (ESI) for $C_{17}H_8Cl_2F_4N_4S$ (M^+) calcd.: 445.9783; found: 445.9782.

5-Amino-1-[2-chloro-4-(trifluoromethyl)phenyl]-4-phenythio-1H-pyrazole-3-carbonitrile (3ba)

White solid, mp 136–137 °C (uncorrected); ^1H NMR (300 MHz, actone-d_6) δ: 7.30 (s, 1H), 7.17–7.10 (m, 2H), 6.49–6.31 (m, 5H), 5.25 (brs, 2H); ^{13}C NMR (125 MHz, actone-d_6) δ: 153.3, 137.9, 136.5, 132.8, 132.3 (2C), 129.9 (q, $J = 45.0$ Hz, 1C), 129.7, 128.7, 128.6, 126.7 (2C), 126.6, 122.8 (q, $J = 271.3$ Hz, 1C), 113.7, 102.3, 90.7; LRMS (EI, 70 eV) m/z (%): 394 (M^+, 100). HRMS (ESI) for $C_{17}H_{10}ClF_3N_4S$ (M^+) calcd.: 394.0267; found: 394.0270.

5-Amino-1-[2-chloro-4-(trifluoromethyl)phenyl]-4-(4-methoxyphenyl) thio-1H-pyrazole-3-carbonitrile (3bc)

White solid, mp 130–131 °C (uncorrected); ^1H NMR (300 MHz, actone-d_6) δ: 8.07 (s, 1H), 7.97–7.89 (m, 2H), 7.23 (d, $J = 9.0$ Hz, 2H), 6.87 (d, $J = 9.0$ Hz, 2H), 6.02 (brs, 2H), 3.74 (s, 3H); ^{13}C NMR (125 MHz, actone-d_6) δ: 159.7, 152.8, 137.8, 136.6, 132.8, 132.0, 130.9 (q, $J = 33.4$ Hz, 1C), 130.3 (2C), 129.6, 128.6, 128.1, 124.1 (q, $J = 270.3$ Hz, 1C), 115.8 (2C), 113.9, 93.3, 55.7; LRMS (EI, 70 eV) m/z (%): 424 (M^+, 100). HRMS (ESI) for $C_{18}H_{12}ClF_3N_4OS$ (M^+) calcd.: 424.0374; found: 424.0374.

5-Amino-1-[2-chloro-5-(trifluoromethyl)phenyl]-4-phenylthio-1H-pyrazole-3-carbonitrile (3ca)

White solid, mp 142–143 °C (uncorrected) (lit.[1] mp 136–137 °C); ^{1}H NMR (300 MHz, actone-d_6) δ: 7.28 (s, 1H), 7.15–7.08 (m, 2H), 6.47–6.29 (m, 5H), 5.22 (brs, 2H); ^{13}C NMR (125 MHz, actone-d_6) δ: 153.3, 137.9, 136.5, 132.8, 132.3, 131.2, 130.8 (q, J= 33.5 Hz, 1C), 130.1 (2C), 129.7, 128.6, 126.7 (2C), 126.6, 124.3 (q, J=270.4 Hz, 1C), 113.7, 90.8; LRMS (EI, 70 eV) m/z (%): 394 (M^+, 100). HRMS (ESI) for $C_{17}H_{10}ClF_3N_4S$ (M^+) calcd.: 394.0267; found: 394.0266.

5-Amino-1-[2-chloro-5-(trifluoromethyl)phenyl]-4-(4-methoxyphenyl) thio-1H-pyrazole-3-carbonitrile (3cc)

White solid, mp 127–129 °C (uncorrected); ^{1}H NMR (300 MHz, actone-d_6) δ: 7.22 (s, 1H), 7.12–7.05 (m, 2H), 6.39 (d, J = 9.0 Hz, 2H), 6.03 (d, J = 9.0 Hz, 2H), 5.17 (brs, 2H), 2.89 (s, 3H); ^{13}C NMR (125 Hz, actone-d_6) δ: 159.8, 152.7, 137.8, 136.6, 132.8, 132.0, 131.3 (q, J = 33.4 Hz, 1C), 130.2 (2C), 129.6, 128.5, 128.0, 125.3, 122.1 (q, J = 270.5 Hz, 1C), 115.7, 113.8, 93.2, 55.6; LRMS (EI, 70 eV) m/z (%): 424 (M^+, 100). HRMS (ESI) for $C_{18}H_{12}ClF_3N_4OS$ (M^+) calcd.: 424.0374; found: 424.0375.

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-phenylselanyl-1H-pyrazole-3-carbonitrile (4ai)

White oil; ^{1}H NMR (300 MHz, actone-d_6) δ: 8.11 (s, 2H), 7.32–7.23 (m, 5H), 6.15 (brs, 2H); ^{13}C NMR (125 MHz, actone-d_6) δ: 153.4, 137.4 (2C), 137.0, 134.7 (q, J = 33.8 Hz, 1C), 134.0, 132.8, 132.0, 130.3 (2C), 129.2 (2C), 127.3 (2C), 123.3 (q, J = 271.4 Hz, 1C), 113.9, 85.6; LRMS (EI, 70 eV) m/z (%): 476 (M^+, 100). HRMS (ESI) for $C_{17}H_9Cl_2F_3N_4Se$ (M^+) calcd.: 475.9322; found: 475.9321.

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-benylselanyl-1H-pyrazole-3-carbonitrile (4aj)

White solid, mp 153–155 °C (uncorrected); ^{1}H NMR (300 MHz, actone-d_6) δ: 8.05 (s, 2H), 7.25–7.19 (m, 5H), 5.64 (brs, 2H), 3.96 (s, 2H); ^{13}C NMR (125 MHz, actone-d_6) δ: 153.0, 139.7, 137.4 (2C), 137.2, 134.5 (q, J = 33.8 Hz, 1C), 134.1, 129.9 (2C), 129.3 (2C), 127.7 (2C), 127.4, 123.4 (q, J = 271.3 Hz, 1C), 114.1, 86.0, 32.3; LRMS (EI, 70 eV) m/z (%): 490 (M^+, 100). HRMS (ESI) for $C_{18}H_{11}Cl_2F_3N_4Se$ (M^+) calcd.: 489.9478; found: 489.9477.

5-Amino-1-[2-chloro-4-(trifluoromethyl)phenyl]-4-Phenylselanyl-1H-pyrazole-3-carbonitrile (4bi)

Yellow solid, mp 139–140 °C (uncorrected); ^{1}H NMR (300 MHz, actone-d_6) δ: 8.12 (s, 1H), 8.02–7.82 (m, 2H), 7.37–7.26 (m, 5H), 5.96 (brs, 2H); ^{13}C NMR (125 MHz, actone-d_6) δ: 153.4, 137.8, 136.6, 133.0, 132.8, 132.7, 131.0 (q, J = 33.5 Hz, Hz, 1C), 130.3 (2C), 129.6 (2C), 129.5, 128.5 (2C), 125.5 (q, J = 270.3 Hz, 1C), 114.2,

85.9; LRMS (EI, 70 eV) m/z (%): 442 (M^+, 100). HRMS (ESI) for $C_{17}H_{10}ClF_3N_4Se$ (M^+) calcd.: 441.9711; found: 441.9710.

5-Amino-1-[2-chloro-4-(trifluoromethyl)phenyl]-4-Benzylselanyl-1H-pyrazole-3-carbonitrile (4bj)

Yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.75–7.61 (m, 3H), 7.26–7.1 (m, 5H), 3.88 (brs, 2H), 3.69 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 150.7, 138.6, 135.7, 135.1, 132.8, 131.6, 130.9 (q, $J = 33.7$ Hz, 1C), 128.9 (2C), 128.5 (2C), 128.3, 127.1, 126.9, 122.7 (q, $J = 271.1$ Hz, 1C), 112.9, 88.3, 32.5; LRMS (EI, 70 eV) m/z (%): 456 (M^+, 100). HRMS (ESI) for $C_{18}H_{12}ClF_3N_4Se$ (M^+) calcd.: 455.9868; found: 455.9871.

5-Amino-1-[2-chloro-5-(trifluoromethyl)phenyl]-4-Phenylselanyl-1H-pyrazole-3-carbonitrile (4ci)

Brown solid; mp 154–155 °C (uncorrected); ^{1}H NMR (300 MHz, actone-d_6) δ: 8.13–7.98 (m, 3H), 7.38–7.24 (m, 5H), 5.97 (brs, 2H); ^{13}C NMR (125 MHz, actone-d_6) δ: 153.4, 137.8, 136.6, 133.1, 132.8 (2C), 131.0 (q, $J = 33.5$ Hz, 1C), 130.3 (2C), 129.6 (2C), 129.5, 128.5, 127.4, 124.2 (q, $J = 270.1$ Hz, 1C), 114.2, 86.0; LRMS (EI, 70 eV) m/z (%): 442 (M^+, 100). HRMS (ESI) for $C_{17}H_{10}ClF_3N_4Se$ (M^+) calcd.: 441.9711; found: 441.9713.

5-Amino-1-[2-chloro-5-(trifluoromethyl)phenyl]-4-Benzylselanyl-1H-pyrazole-3-carbonitrile (4cj)

Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.75–7.61 (m, 3H), 7.24–7.11 (m, 5H), 4.12 (brs, 2H), 3.7 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 150.7, 138.6, 135.7, 135.1, 132.8, 131.6, 130.8 (q, $J = 33.7$ Hz, 1C), 128.9 (2C), 128.5 (2C), 128.3, 127.1, 127.0, 122.3 (q, $J = 271.1$ Hz, 1C), 112.9, 88.3, 32.5, 141.3, 139.4, 135.5, 130.3, 128.8, 125.6, 124.6, 122.2, 120.7, 119.0, 110.8, 99.2, 12.1; LRMS (EI, 70 eV) m/z (%): 456 (M^+, 100). HRMS (ESI) for $C_{18}H_{12}ClF_3N_4Se$ (M^+) calcd.: 455.9868; found: 455.9869.

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