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Suzuki–Miyaura reactions of *N*-protected tribromopyrazoles. Efficient and site-selective synthesis of 3,4,5-triaryl-pyrazoles, 3,5-diaryl-4-bromopyrazoles and 5-aryl-3,4-dibromopyrazoles

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ABSTRACT

Suzuki–Miyaura reactions of *N*-protected tribromopyrazoles were studied. The reactions proceed with excellent site-selectivity. The first attack occurs at position 5, while the second and third attack occur at positions 3 and 4, respectively. A variety of 3,4,5-triaryl-pyrazoles, 3,5-diaryl-4-bromopyrazoles, and 5-aryl-3,4-dibromopyrazoles were efficiently prepared. The products are not readily available by other methods.

1. Introduction

Pyrazoles are of considerable importance in medicinal chemistry and are also used as synthetic building blocks.[1–6] Pyrazole derivatives, specifically 1-phenylpyrazole derivatives, are known to have a broad spectrum of biological activities. For example, 4-amino-*N*-(1-phenyl-1*H*-pyrazol-5-yl)benzensulfonamide (sulfaphenazole) derived from 5-amino-1-phenylpyrazole is a potent antibacterial drug,[7] while 3-cyano-*N*-(1,3-diphenyl-1*H*-pyrazol-5-yl)benzamide (CDPPD) has been identified as a positive allosteric metabotropic modulator of the glutamate receptor (Fig. 1).[8] Nonsteroidal anti-inflammatory drugs, such as lonazolac are (1,3-diphenyl-1*H*-pyrazol-4-yl)acetic acid derivatives.[9] The anti-inflammatory activity is also typical for (1,4-diphenylpyrazol-3-yl) acetic acid and related compounds.[10] A number of synthetic approaches to pyrazoles have been reported. They have been prepared by 1,3-dipolar cycloaddition of diazoalkanes with alkynes,[11] by cyclization of hydrazines with 1,3-diketones and α,β-unsaturated ketones.[12] The reaction of hydrazines with 4-aryl-2,4-dioxoesters afforded 5-arylpyrazole-3-carboxylates which were transformed into potent and selective COX-1 and COX-2 inhibitors.[13] Pyrazoles have also been prepared by cyclization of dilithiated hydrazones with esters, acid chlorides, nitriles, α-haloketones, propiolates, Weinreb amides and diethyl oxalate.[14]

In recent years, site-selective cross-coupling reactions of polyhalogenated heterocycles have gained increasing importance.[15,16] Site-selective Suzuki–Miyaura (S–M) reactions of tribromopyrroles have been previously reported.[17] A modular approach to various trisubstituted pyrazoles has been reported which is based on sequential direct lithiation of the 3- and 5-positions of the pyrazole ring and their conversion into pyrazolylboronic acids.[18a] The latter was reacted in S–M reactions. Another very interesting synthesis relies on the combination of C–H activation and S–M reactions of monobrominated SEM-protected pyrazoles.[18b] While site-selective metal–halide exchange reactions of *N*-protected tribromopyrazoles are known,[19] palladium catalyzed transformations were unknown until our recent short communication in this field.[20] Herein, we report full details of Suzuki–Miyaura reactions of *N*-protected tribromopyrazoles. These reactions provide

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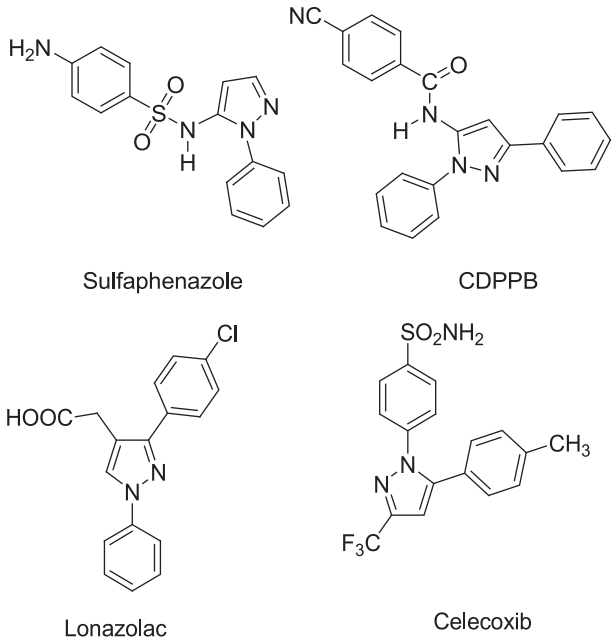
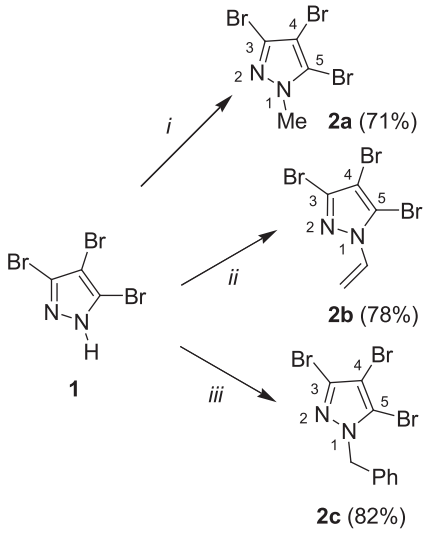


Fig. 1. Some pharmaceuticals bearing a pyrazole moiety.

a convenient approach to triaryl-pyrazoles, 3,5-diaryl-4-bromopyrazoles and 5-aryl-3,4-dibromo-pyrazoles, which are of considerable pharmacological relevance.[21] The products are not readily available by other methods.

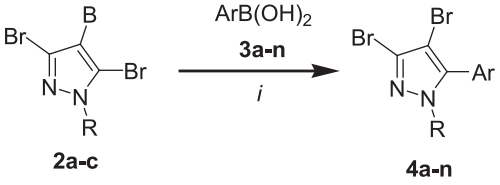
2. Results and discussion

N-Methyl-tribromopyrazole (**2a**) was prepared by reaction of commercially available tribromopyrazole (**1**) with methyl iodide (Scheme 1). *N*-Benzyl-tribromopyrazole (**2c**) was prepared following a known procedure, which was slightly modified.[22] Instead of benzylchloride, benzylbromide was used. *N*-Vinyl-tribromopyrazole (**2b**) was prepared by reaction of **1** with dibromoethane.



Scheme 1. Synthesis of **2a**–**c**. Reagents and conditions: (i) **1** (1.0 equiv), methyl iodide (1.0 equiv), NEt_3 (1.1 equiv), CH_2Cl_2 (5 mL per mmol of 1), 20 °C, 8 h. (ii) **1** (1.0 equiv), 1,2-dibromoethane (1.2 equiv), NEt_3 (5 mL per mmol), CH_3CN (5 mL per mmol of 1), 70 °C, 7 h. (iii) **1** (1.0 equiv), benzylbromide (1.0 equiv), NEt_3 (1.1 equiv), CH_2Cl_2, 20 °C, 4 h.

The Suzuki–Miyaura reaction of **2a**–**c** with arylboronic acids **3a**–**n** (1.1 equiv) afforded the 5-aryl-3,4-dibromopyrazoles **4a**–**n** in 66–81% yield (Table 1, Scheme 2). The reactions were carried out using $Pd(PPh_3)_4$ (3 mol %) as the catalyst. Potassium phosphate (1.5 equiv) was employed as the base. The stoichiometry played an important role (use of 1.0 equiv of the arylboronic acid). The reactions were carried out in a 4:1 mixture of dioxane and water because of the low solubility of the boronic acids in toluene. The employment of $PdCl_2(PPh_3)_2$ or of $Pd(OAc)_2$ in the presence of XPhos, a biaryl ligand developed by Buchwald and Billingsley,[23] gave lower yields. The reaction mixtures were stirred at 100 °C for 12 h. The conversion was not complete when the reaction time was shortened or when the temperature was decreased.



Scheme 2. Synthesis of 5-aryl-3,4-dibromopyrazoles **4a**–**n**. Reagents and conditions: i, **2a**–**c** (1.0 equiv), $ArB(OH)_2$ (1.1 equiv), 2 M K_2CO_3, $Pd(PPh_2)Cl_2$ (3 mol %), 1,4-dioxane/H_2O (4:1), 60 °C, 4 h.

Table 1
Synthesis of **4a**–**n**

3,4	2	R	Ar	% (**4**)[a]
a	**a**	Me	4-MeC_6H_4	76
b	**a**	Me	4-EtC_6H_4	79
c	**a**	Me	4-$^tBuC_6H_4$	81
d	**a**	Me	3-ClC_6H_4	73
e	**a**	Me	4-ClC_6H_4	71
f	**a**	Me	4-FC_6H_4	75
g	**a**	Me	4-$(MeO)C_6H_4$	71
h	**b**	Vinyl	4-MeC_6H_4	66
i	**b**	Vinyl	2-$(MeO)C_6H_4$	69
j	**b**	Vinyl	4-$(MeO)C_6H_4$	73
k	**b**	Vinyl	2,6-$(MeO)_2C_6H_3$	71
l	**c**	Benzyl	3,5-$Me_2C_6H_3$	74
m	**c**	Benzyl	4-FC_6H_4	71
n	**c**	Benzyl	4-$(MeO)C_6H_4$	76

[a] Yields of isolated compounds.

The formation of **4a**–**n** proceeded with excellent site-selectivity in favour of position 5. Inspection of the crude product mixture showed that a small amount of pyrazole derived from double and triple Suzuki reaction were formed. In addition, some biaryl formation (by dimerization of the boronic acid) was detected. A good yield was obtained even for product **4k** derived from a sterically hindered arylboronic acid. No clear dependence of the yields from the electronic nature of the arylboronic acid was observed.

The configuration of the products was unambiguously confirmed by 2D NMR experiments (NOESY, HMQC). For example, the regioselectivity of compound **4a** was established unambiguously by 2D NMR using ^1H–^1H NOESY and HMQC experiments. The methyl protons (NMe) at δ=3.70 show a clear correlation through space with the phenyl protons at δ=7.24, which confirm that the 4-methylphenyl group is attached to C-5 of the pyrazole moiety (Fig. 2).

Likewise, the structure of compound **4j** was established by 2D NMR. The vinylic proton attached to carbon C-129.7 showed a clear correlation through space with the phenyl proton located at δ 7.30, which confirmed that the 4-methoxyphenyl is attached at C-5 of the pyrazole moiety (Fig. 3).

The structure of **4n** was independently confirmed by an X-ray crystal structure analysis (Fig. 4).[24]

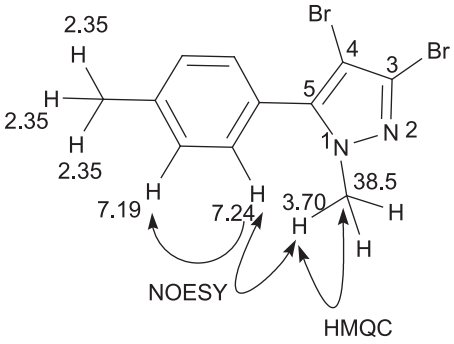


Fig. 2. 2D NMR correlations (HMQC and NOSEY) of **4a**.

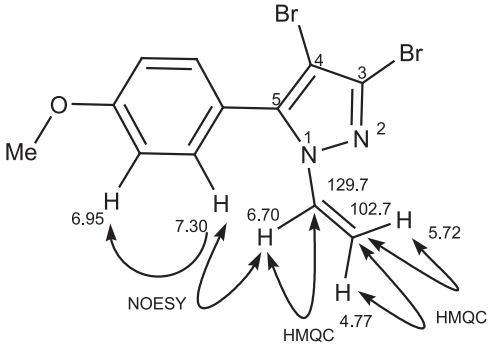


Fig. 3. 2D NMR correlations (HMQC and NOSEY) of **4j**.

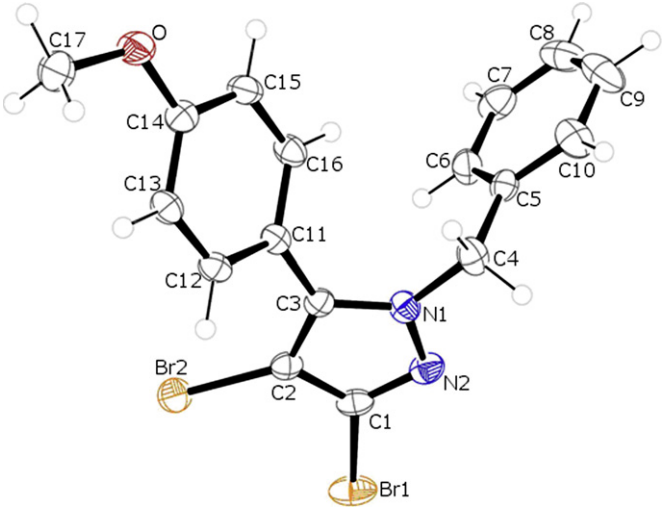
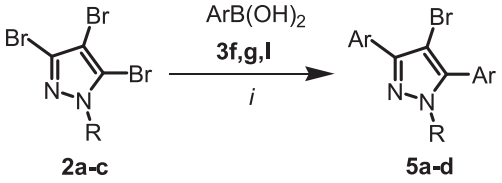


Fig. 4. ORTEP plot of **4n** (50% probability level).

The Suzuki–Miyaura reaction of **2a**–**c** with arylboronic acids **3f**,**g**,**l** (2.2 equiv) afforded the 3,5-diaryl-4-bromopyrazoles **5a**–**d** in 60–66% yield (Table 2, Scheme 3). During the optimization, it proved to be important to slightly increase the amount of the catalyst (5 mol %) and to use exactly 2 equiv of the boronic acid and 3.0 equiv of base. The yields decreased when $Pd(OAc)_2$/XPhos or $PdCl_2(PPh_3)_2$ were employed. Reduced yields were also obtained when the temperature was decreased or when the reaction time was shortened. A small amount of monoarylated and triarylated pyrazole was formed as side product (inspection of the crude product mixture). The structure of **5c** was previously confirmed by an X-ray crystal structure analysis.[20]



Scheme 3. Synthesis of 5-aryl-3,4-dibromopyrazoles **5a**–**d**. Reagents and conditions: i, **2a**–**c** (1.0 equiv), $ArB(OH)_2$ (2.2 equiv), 2 M K_2CO_3, $Pd(PPh_2)Cl_2$ (5 mol %), 1,4-dioxane/H_2O (4:1), 80 °C, 6 h.

Table 2
Synthesis of **5a**–**d**

5	3	R	Ar	% (5)[a]
a	**g**	Me	4-(MeO)C_6H_4	60
b	**l**	Vinyl	3,5-$Me_2C_6H_3$	62
c	**g**	Vinyl	4-(MeO)C_6H_4	60
d	**f**	Benzyl	4-FC_6H_4	66

[a] Yields of isolated compounds.

Suzuki reactions of *N*-protected tribromopyrazoles with 3.3 equiv of arylboronic acids were next studied. As a test reaction for the optimization studies, the synthesis of **6a** was investigated. Initially, it was found that mixtures of products were formed when $Pd(PPh_3)_4$ (3 mol %) or $Pd(PPh_3)_2Cl_2$ were used as the catalysts. In contrast, good yields of pure triarylated products were obtained when $Pd(OAc)_2$ (5 mol %) in the presence of XPhos (10 mol %) was used as the catalyst (dioxane, 90 °C, 6 h) (entry 4, Table 3). The best yields were obtained when $Pd(OAc)_2$ (5 mol %) was used in the presence of SPhos (10 mol %) in an aqueous solution of K_2CO_3 (2 M) (entry 3, Table 3).

The Suzuki–Miyaura reaction of **2a**–**c** with an excess of arylboronic acids **3a**–**c**,**e**–**g**,**l**,**m** (3.5 equiv) afforded the 3,4,5-triarylpyrazoles **6a**–**m** in 66–91% yield (Table 4, Scheme 4). The yields of the products derived from methyl derivative **2a** were generally higher than those of **2b** and **2c**, which might be explained by the high stability of the methyl group. No clear trend was observed for the dependence of the yields from the type of arylboronic acid employed. Inspection of the crude product mixture showed that a small amount of biaryls were formed.

The reaction of 5-aryl-3,4-dibromopyrazoles **4** with arylboronic acids **3a**,**b**,**d**,**g**,**o** afforded the 3,4,5-triaryl-pyrazoles **7a**–**i** in

Scheme 4. Synthesis of 3,4,5-triaryl-pyrazoles **6a**–**m**. Reagents and conditions: i, **1** (1.0 equiv), $ArB(OH)_2$ (3.3 equiv), 2 M K_2CO_3,, $Pd(OAc)_2$ (5 mol %), SPhos (10 mol %), 1,4-dioxane/H_2O (4:1), 100 °C, 8 h.

Table 3
Optimization of the synthesis of 1-methyl-3,4,5-tri(4-methylphenyl)pyrazole (**6a**)

Entry	Conditions	% (6a)[a]
1	$Pd(PPh_3)_2Cl_2$ (5 mol %), aq K_2CO_3 (2 M)	42
2	$Pd(PPh_3)_4$ (5 mol %), aq K_2CO_3 (2 M)	28
3	$Pd(OAc)_2$ (5 mol %), SPhos (10 mol %), aq K_2CO_3 (2 M)	91
4	$Pd(OAc)_2$ (5 mol %), XPhos (10 mol %), aq K_2CO_3 (2 M)	80
5	$Pd(OAc)_2$ (5 mol %), $(EtOH)_3N$, K_2CO_3 (2 M)	Decomp.
6	$Pd(OAc)_2$ (5 mol %), $(EtO)_2PPh$, K_2CO_3 (2 M)	Traces
7	$Pd(OAc)_2$ (5 mol %), $(^nBu)_3P$, K_2CO_3 (2 M)	20

[a] Yields of isolated compounds.

Table 4
Synthesis of **6a**–**m**

6	3	R	Ar	% (**6**)[a]
a	**a**	Me	4-MeC_6H_4	91
b	**b**	Me	4-EtC_6H_4	89
c	**c**	Me	4-$^tBuC_6H_4$	86
d	**l**	Me	3,5-$Me_2C_6H_3$	84
e	**m**	Me	4-FC_6H_4	87
f	**g**	Me	4-$(MeO)C_6H_4$	81
g	**b**	Vinyl	4-EtC_6H_4	66
h	**c**	Vinyl	4-$^tBuC_6H_4$	73
i	**l**	Vinyl	3,5-$Me_2C_6H_3$	71
j	**e**	Benzyl	4-ClC_6H_4	76
k	**f**	Benzyl	4-FC_6H_4	78
l	**a**	Benzyl	4-MeC_6H_4	81
m	**b**	Benzyl	4-EtC_6H_4	84

[a] Yields of isolated compounds.

74–92% yield (Scheme 5, Table 5). The best yields were obtained when $Pd(OAc)_2$ (5 mol %)/SPhos (10 mol %) was used as the catalyst.

Scheme 5. Synthesis of **7a**–i. Reagents and conditions: (i) **4** (1.0 equiv), $ArB(OH)_2$ (2.2 equiv), K_2CO_3 (2 M, 1 mL), $Pd(OAc)_2$ (5 mol %), SPhos (10 mol %), 1,4-dioxane/H_2O (4:1), 100 °C, 6 h.

Table 5
Synthesis of **7a**–**i**

7	3	Ar^1	Ar^2	% (**7**)[a]
a	**o**	4-MeC_6H_4	C_6H_5	92
b	**g**	4-MeC_6H_4	4-$(MeO)C_6H_4$	84
c	**o**	4-EtC_6H_4	C_6H_5	89
d	**d**	4-EtC_6H_4	3-ClC_6H_5	82
e	**g**	4-EtC_6H_4	4-$(MeO)C_6H_4$	86
f	**o**	4-ClC_6H_4	C_6H_5	79
g	**b**	4-ClC_6H_4	4-EtC_6H_4	81
h	**a**	4-$(MeO)C_6H_4$	4-MeC_6H_4	83
i	**g**	4-$(MeO)C_6H_4$	3-ClC_6H_4	74

[a] Yields of isolated products.

The structure of **7a** was independently confirmed by X-ray crystal structure (Fig. 5).[24]

In conclusion, we have reported site-selective Suzuki–Miyaura reactions of *N*-protected tribromopyrazoles. The first attack occurs at position 5, while the second and third attack occur at positions 3 and 4, respectively. The higher reactivity of carbon atoms C-3 and C-5 compared to C-4 can be explained by their location next to the nitrogen atom and, thus, more electron deficient character. The higher reactivity of position 5 compared to 3 is surprising because position 5 is sterically more hindered than position 3. The selectivity might again be explained by electronic reasons. A variety of 3,4,5-triaryl-pyrazoles, 3,5-diaryl-4-bromopyrazoles and 5-aryl-3,4-dibromopyrazoles were efficiently prepared which are not readily available by other methods.

3. Experimental section

3.1. General procedure

To a 1,4-dioxane solution (4 mL) of **2a**,**b**,**c** (0.5 mmol) were added $Pd(PPh_3)_4$ (3–5 mol %) or $Pd(OAc)_2$ (5 mol %) and SPhos (10 mol %), at 20 °C under argon atmosphere. After stirring for 30 min, the arylboronic acid (2 M aqueous solution of K_2CO_3) was added. The mixture was heated for 6–8 h at 60–100 °C. After cooling to 20 °C, the mixture was diluted with H_2O, extracted with CH_2Cl_2 (3×25 mL), dried (Na_2SO_4) and filtered. The solvent of the filtrate was concentrated in vacuo and the residue was purified by column chromatography (heptanes/EtOAc).

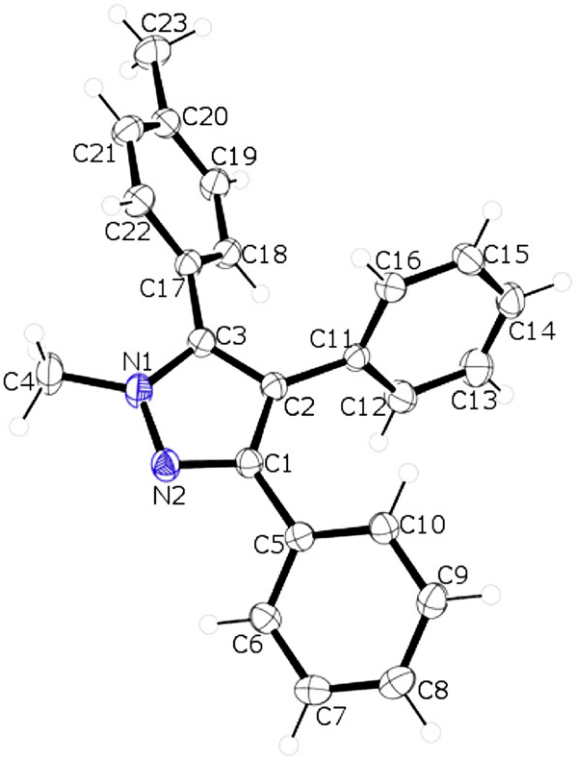


Fig. 5. ORTEP plot of **7a** (50% probability level).

*3.1.1. 3,4-Dibromo-1-methyl-5-p-tolyl-1H-pyrazole (**4a**).* Starting with **2a** (159 mg, 0.5 mmol), $Pd(PPh_3)_2Cl_2$ (10 mg, 3 mol %), K_2CO_3 (H_2O, 2 M, 0.5 mL) and *p*-tolylboronic acid (75 mg, 0.55 mmol), **4a** was isolated as a white solid (125 mg, 76%). Mp=56–57 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=2.35 (s, 3H, CH_3), 3.70 (s, 3H, NCH_3), 7.19 (d, 2H, J=8.5 Hz, ArH), 7.24 (d, 2H, J=8.5 Hz, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=21.4 (CH_3), 38.5 (NCH_3), 96.2, 125.0, 127.1 (C), 129.5, 129.6 (CH), 139.9, 143.3 (C). IR (KBr): ν=2948, 2918, 2852 (w), 1484, 1361, 1273, 995 (m), 823 (s), 720 (w), 575 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=330 ([M, ^{81}Br, $^{79}Br]^+$, 100), 328 ([M, $^{79}Br_2]^+$, 51), 170 (10), 169 (10). HRMS (EI, 70 eV): calcd for $C_{11}H_{10}N_2Br_2$ (M^+, ^{81}Br, ^{79}Br]): 329.91848; found 329.919092.

*3.1.2. 3,4-Dibromo-5-(4-ethylphenyl)-1-methyl-1H-pyrazole (**4b**).* Starting with **2a** (159 mg, 0.5 mmol), $Pd(PPh_3)_2Cl_2$ (10 mg, 3 mol %), K_2CO_3 (H_2O, 2 M, 0.5 mL) and 4-ethylphenylboronic acid (82 mg, 0.55 mmol), **4b** was isolated as a white solid (136 mg, 79%). Mp=61 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=1.20 (t, J=7.4 Hz, CH_3), 2.63 (q, J=7.6 Hz, CH_2), 3.69 (s, 3H, NCH_3), 7.20 (d, J=8.4 Hz, 2H, ArH), 7.25 (d, J=8.4 Hz, 2H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=15.2 (CH_3), 28.7 (CH_2), 38.5 (NCH_3), 96.2, 125.1, 127.1 (C), 128.3, 129.5 (CH), 143.3, 146.0 (C). IR (KBr): ν=2963 (m), 2929, 2848 (w), 1613 (m), 1485 (m), 1363 (s), 1274, 1117, 1004 (m) 994, 837 (s), 791, 613 (w), 577 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=344 ([M, ^{81}Br,

$^{79}Br]^+$, 100), 342 ([M, $^{79}Br_2]^+$, 51), 331 (37), 329 (75), 327 (38). HRMS (ESI$^+$): calcd for $C_{12}H_{13}Br_2N_2$ ([M+H]$^+$, $^{79}Br_2$): 342.9440; found 342.9442.

*3.1.3. 3,4-Dibromo-5-(4-tert-butylphenyl)-1-methyl-1H-pyrazole (**4c**).* Starting with **2a** (159 mg, 0.5 mmol), $Pd(PPh_3)_2Cl_2$ (10 mg, 3 mol %), K_2CO_3 (H_2O, 2 M, 0.5 mL) and 4-*tert*-butylphenylboronic acid (98 mg, 0.55 mmol), **4c** was isolated as a white solid (151 mg, 81%). Mp=61 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=1.29 (s, 9H, $3CH_3$), 3.72 (s, 3H, NCH_3), 7.25 (d, J=7.1 Hz, 2H, ArH), 7.44 (d, J=6.9 Hz, 2H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=31.2 (CH_3), 34.8 (C), 38.6 (NCH_3), 96.2, 124.9 (C), 125.7 (CH), 127.2 (C), 129.2 (CH), 143.3, 152.8 (C). IR (KBr): ν=3031, 2954, 2865 (w), 1680 (m), 1363 (m), 1266 (s), 1109 (m), 994, 839 (s), 694 (m), 587 (s) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=372 ([M, ^{81}Br, $^{79}Br]^+$, 48), 370 ([M, $^{79}Br_2]^+$, 27), 359 (45), 358 (11), 357 (100), 356 (13), 355 (54), 329 (18), 164 (17). HRMS (ESI$^+$): calcd for $C_{14}H_{17}Br_2N_2$ ([M+H]$^+$, $^{79}Br_2$): 370.9753; found 370.9751.

*3.1.4. 3,4-Dibromo-5-(3-chlorophenyl)-1-methyl-1H-pyrazole (**4d**).* Starting with **2a** (159 mg, 0.5 mmol), $Pd(PPh_3)_2Cl_2$ (10 mg, 3 mol %), K_2CO_3 (H_2O, 2 M, 0.5 mL) and 3-chlorophenylboronic acid (86 mg, 0.55 mmol), **4d** was isolated as a white solid (129 mg, 73%). Mp=67 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=3.73 (s, 3H, NCH_3), 7.20–7.23 (m, 1H, ArH), 7.31–7.33 (m, 1H, ArH), 7.38 (s, 1H, ArH), 7.39–7.40 (m, 1H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=38.7 (NCH_3), 96.8, 125.7, 127.4 (C), 127.8, 129.6, 129.9, 130.2 (CH), 134.8, 141.8 (C). IR (KBr): ν=3059, 2945, 2926, 2850 (w), 1600, 1565, 1461, 1366, 1272, 1080, 996, 897 (m), 784 (s), 686 (s), 593 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=350 ([M, ^{81}Br, $^{79}Br]^+$, 100), 348 ([M, $^{79}Br_2]^+$, 45), 147 (10). HRMS (ESI$^+$): calcd for $C_{10}H_8Br_2ClN_2$ ([M+H]$^+$, $^{79}Br_2$): 348.8737; found 348.874.

*3.1.5. 3,4-Dibromo-5-(4-chlorophenyl)-1-methyl-1H-pyrazole (**4e**).* Starting with **2a** (159 mg, 0.5 mmol), $Pd(PPh_3)_2Cl_2$ (10 mg, 3 mol %), K_2CO_3 (H_2O, 2 M, 0.5 mL) and 4-chlorophenylboronic acid (86 mg, 0.55 mmol), **4e** was isolated as a white solid (125 mg, 71%). Mp=52–53 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=3.69 (s, 3H, NCH_3), 7.26 (d, J=8.5 Hz, 2H, ArH), 7.42 (d, J=8.5 Hz, 2H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=38.6 (NCH_3), 96.6, 126.3, 127.3 (C), 129.2, 130.9 (CH), 136.0, 142.1 (C). IR (KBr): ν=3028, 2952, 2851 (w), 1473, 1359, 1264, 1089 (m), 996, 836 (s), 775, 715, 644, 574 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=350 ([M, ^{81}Br, $^{79}Br]^+$, 100), 348 ([M, $^{79}Br_2]^+$, 45), 147 (11). HRMS (ESI$^+$): calcd for $C_{10}H_8Br_2ClN_2$ ([M+H]$^+$, $^{79}Br_2$): 348.8736; found 348.873.

*3.1.6. 3,4-Dibromo-5-(4-fluorophenyl)-1-methyl-1H-pyrazole (**4f**).* Starting with **2a** (159 mg, 0.5 mmol), $Pd(PPh_3)_2Cl_2$ (10 mg, 3 mol %), K_2CO_3 (H_2O, 2 M, 0.5 mL) and 4-fluorophenylboronic acid (77 mg, 0.55 mmol), **4f** was isolated as a white solid (125 mg, 75%). Mp=55–56 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=3.71 (s, 3H, NCH_3), 7.13–7.19 (m, 2H, ArH), 7.28–7.34 (m, 2H, ArH). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−110.1. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=38.5 (NCH_3), 96.6 (C), 116.1 (d, $J_{F,C}$=21.8 Hz, CH), 123.9 (d, $J_{F,C}$=3.2 Hz, C), 127.2 (C), 131.6 (d, $J_{F,C}$=10.8 Hz, CH), 142.3 (C), 163.4 (d, $J_{F,C}$=244.7 Hz, C–F). IR (KBr): ν=3038, 2951, 2855 (w), 1730 (w), 1606, 1541 (m), 1484, 1361, 1219 (s), 1159, 997 (m), 839 (s), 816, 721, 611, 575 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=334 ([M, ^{81}Br, $^{79}Br]^+$, 100), 332 ([M, $^{79}Br_2]^+$, 79), 174, 136 (11), 131 (12). HRMS (ESI$^+$): calcd for $C_{10}H_8Br_2FN_2$ ([M+H]$^+$, ^{81}Br, ^{79}Br): 334.9013; found 334.9016.

*3.1.7. 3,4-Dibromo-5-(4-methoxyphenyl)-1-methyl-1H-pyrazole (**4g**).* Starting with **2a** (159 mg, 0.5 mmol), $Pd(PPh_3)_2Cl_2$ (10 mg, 3 mol %), K_2CO_3 (H_2O, 2 M, 0.5 mL) and 4-methoxyphenylboronic acid (83 mg, 0.55 mmol), **4g** was isolated as a white solid (123 mg, 71%). Mp=73 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=3.67 (s, 3H, CH_3), 3.78 (s, 3H, CH_3), 6.93 (d, J=8.8 Hz, 2H, ArH), 7.23 (d, J=8.8 Hz, 2H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=37.5 (NCH_3), 54.3 (OCH_3), 95.2 (C), 113.2 (CH), 118.9, 126.0 (C), 129.9 (CH), 142.1, 159.5 (C). IR (KBr): ν=3012, 2922, 2839 (w), 1607, 1539, 1481, 1366, 1257, 1176, 1025, 991 (m), 831 (s), 803 (m), 765, 687, 613, 573 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=346 ([M, ^{81}Br, $^{79}Br]^+$, 100), 344 ([M, $^{79}Br_2]^+$, 51), 333 (11), 331 (23), 329 (11). HRMS (ESI$^+$): calcd for $C_{11}H_{11}Br_2N_2$ ([M+H]$^+$, $^{79}Br_2$): 344.9233; found 344.9234.

*3.1.8. 3,4-Dibromo-5-p-tolyl-1-vinyl-1H-pyrazole (**4h**).* Starting with **2b** (165 mg, 0.5 mmol), $Pd(PPh_3)_2Cl_2$ (10 mg, 3 mol %), K_2CO_3 (H_2O, 2 M, 0.5 mL) and *p*-tolylboronic acid (75 mg, 0.55 mmol), **4h** was isolated as a white solid (112 mg, 66%). Mp=67 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=2.34 (s, 3H, CH_3), 4.76 (d, 1H, J=8.1 Hz, vinyl), 5.70 (d, 1H, J=15.0 Hz, vinyl), 6.71 (dd, 1H, J=15.1, 8.7 Hz, vinyl CH), 7.20 (d, 2H, J=8.4 Hz, ArH), 7.23 (d, 2H, J=8.6 Hz, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=21.3 (CH_3), 97.1 (C), 101.8 (CH_2), 114.1 (CH), 125.1, 127.1 (C), 129.3, 128.5 (CH), 138.8, 145.2 (C). IR (KBr): ν=3032, 2987, 2948, 2917, 2850 (w), 1486, 1364, 1276, 993 (m), 827 (s), 726 (w), 579 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=340 ([M, $^{79}Br_2]^+$, 100), 170 (10). HRMS (EI, 70 eV): calcd for $C_{12}H_{10}N_2Br_2$ (M$^+$, [$^{79}Br_2$]): 340.81848; found 340.819092.

*3.1.9. 3,4-Dibromo-5-(2-methoxyphenyl)-1-vinyl-1H-pyrazole (**4i**).* Starting with **2b** (165 mg, 0.5 mmol), $Pd(PPh_3)_2Cl_2$ (10 mg, 3 mol %), K_2CO_3 (H_2O, 2 M, 0.5 mL) and 2-methoxyphenylboronic acid (83 mg, 0.55 mmol), **4i** was isolated as a white solid (122 mg, 69%). Mp=58–59 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=3.78 (s, 3H, OCH_3), 4.78 (d, 1H, J=8.7 Hz, vinyl), 5.74 (d, 1H, J=15.2 Hz, vinyl), 6.72 (dd, 1H, J=15.2, 8.6 Hz, vinyl CH), 6.94–6.98 (m, 2H, ArH), 7.29–7.31 (m, 1H, ArH), 8.31–8.33 (m, 1H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=55.3 (OCH_3), 97.9 (C), 102.8 (CH_2), 114.5 (CH), 119.1 (C), 121.7 (CH), 122.3 (C), 131.5 (CH), 131.7, 152.1 (C). IR (KBr): ν=3012, 2933, 1741 (w), 1645 (m), 1554 (w), 1468 (s), 1422 (m), 1382 (w), 1345 (m), 1322 (s), 1280 (m), 1239 (s), 1186 (w), 1172 (s), 1101 (m), 1027 (s), 983 (s), 887 (m), 832 (s), 602, 550 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=358 ([M, ^{81}Br, $^{79}Br]^+$, 100), 356 ([M, $^{79}Br_2]^+$, 70), 343 (13), 327 (22), 277 (39), 246 (22), 198 (23). HRMS (EI, 70 eV): calcd for $C_{12}H_{10}N_2Br_2O$ [M, $^{79}Br_2]^+$: 355.81523; found 355.815343.

*3.1.10. 3,4-Dibromo-5-(4-methoxyphenyl)-1-vinyl-1H-pyrazole (**4j**).* Starting with **2b** (165 mg, 0.5 mmol), $Pd(PPh_3)_2Cl_2$ (10 mg, 3 mol %), K_2CO_3 (H_2O, 2 M, 0.5 mL) and 4-methoxyphenylboronic acid (83 mg, 0.55 mmol), **4j** was isolated as a white solid (130 mg, 73%). Mp=68–69 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=3.80 (s, 3H, OCH_3), 4.77 (d, 1H, J=8.7 Hz, vinyl), 5.72 (d, 1H, J=15.2 Hz, vinyl), 6.70 (dd, 1H, J=15.2, 8.5 Hz, vinyl CH), 6.95 (d, 2H, J=8.8 Hz, ArH), 7.25 (d, 2H, J=8.8 Hz, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=55.4 (OCH_3), 98.2 (C), 102.7 (CH_2), 114.3 (CH), 119.0 (C), 129.7 (CH), 130.5 (C), 131.5 (CH), 142.4, 160.7 (C). IR (KBr): ν=3002, 2936, 2835, 1730 (w), 1641 (m), 1574 (w), 1488 (s), 1432 (m), 1392 (w), 1355 (m), 1332 (s), 1290 (m), 1249 (s), 1196 (w), 1174 (s), 1110 (m), 1030 (s), 984 (s), 888 (m), 833 (s), 801 (m), 725 (w), 602 (m), 551 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=358 ([M, ^{81}Br, $^{79}Br]^+$, 100), 356 ([M, $^{79}Br_2]^+$, 70), 353 (13), 327 (22), 277 (39), 246 (22), 198 (23). HRMS (EI, 70 eV): calcd for $C_{12}H_{10}N_2Br_2O$ [M, $^{79}Br_2]^+$: 355.91544; found 355.915354.

*3.1.11. 3,4-Dibromo-5-(2,6-dimethoxyphenyl)-1-vinyl-1H-pyrazole (**4k**).* Starting with **2b** (165 mg, 0.5 mmol), $Pd(PPh_3)_2Cl_2$ (10 mg, 3 mol %), K_2CO_3 (H_2O, 2 M, 0.5 mL) and 2,6-dimethoxyphenylboronic acid (100 mg, 0.55 mmol), **4k** was isolated as a white solid (139 mg, 71%). Mp=60–61 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=3.69 (s, 6H, $2OCH_3$), 4.65 (d, 1H, J=8.6 Hz, vinyl), 5.66 (d, 1H, J=15.2 Hz, vinyl), 6.47 (dd, 1H, J=15.2, 8.6 Hz, vinyl CH), 6.57 (d, 2H, J=8.8 Hz, ArH), 7.33–7.39 (m, 1H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$):

δ=55.9 (2OCH_3), 100.0 (C), 101.2 (CH_2), 103.9 (CH), 104.3, 130.0 (C), 130.2, 132.5 (CH), 137.0, 158.8 (C). IR (KBr): ν=3093, 2928, 2838, 1726 (w), 1643 (m), 1537 (w), 1474 (s), 1431 (m), 1389 (w), 1356 (m), 1332 (s), 1297 (w), 1253 (s), 1187, 1173 (w), 1253 (s), 1150 (w), 1107 (s), 1030 (w), 985 (s), 886 (w), 763 (m), 588 (w) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%)=388 ([M, ^{81}Br, $^{79}Br]^+$, 100), 386 ([M, $^{79}Br_2]^+$, 77), 276 (26), 265 (13), 228 (42). HRMS (ESI^+): calcd for $C_{13}H_{13}N_2Br_2O_2$ [(M+H), ^{81}Br, $^{79}Br]^+$: 388.9918; found 388.9326.

*3.1.12. 1-Benzyl-3,4-dibromo-5-(3,5-dimethylphenyl)-1H-pyrazole (**4l**).* Starting with **2c** (197 mg, 0.50 mmol), $Pd(PPh_3)_2Cl_2$ (10 mg, 3 mol %), K_2CO_3 (H_2O, 2 M, 0.5 mL) and 3,5-dimethylphenylboronic acid (82 mg, 0.55 mmol), **4l** was isolated as a white solid (155 mg, 74%). Mp=73–74 °C. ^1H NMR (250 MHz, $CDCl_3$): δ=2.23 (s, 6H, OCH_3), 5.11 (s, 2H, CH_2), 6.76 (s, 2H, ArH), 6.97 (s, 2H, ArH), 7.19–7.23 (m, 5H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=21.2 (s, 6H, $2CH_3$), 54.7 (CH_2), 96.8, 125.3 (C), 127.3, 127.4, 127.7 (CH), 128.0 (C), 128.6, 131.4 (CH), 136.3, 138.4, 143.9 (C). IR (KBr): ν=3029, 2918, 2853 (w), 1603, 1495, 1453 (m), 1356 (s), 1275, 1193, 1077, 1029 (m), 999 (s), 905, 861, 848, 785 (m), 727, 696 (s), 576 (m) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%)=418 ([M, $^{79}Br_2]^+$, 100), 234 (10), 143 (11), 91 (54), 65 (11). HRMS (ESI^+): calcd for $C_{18}H_{17}Br_2N_2$ ($[M+H]^+$, $^{79}Br_2$): 418.9753; found 418.9751.

*3.1.13. 1-Benzyl-3,4-dibromo-5-(4-fluorophenyl)-1H-pyrazole (**4m**).* Starting with **2c** (197 mg, 0.62 mmol), $Pd(PPh_3)_2Cl_2$ (10 mg, 3 mol %), K_2CO_3 (H_2O, 2 M, 0.5 mL) and 4-fluorophenylboronic acid (77 mg, 0.55 mmol), **4m** was isolated as a white solid (144 mg, 71%). Mp=71–72 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=5.11 (s, 2H, CH_2), 7.12–7.15 (m, 2H, 2H, ArH), 7.18–7.23 (m, 5H, ArH), 7.29–7.33 (m, 2H, 2H, ArH). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−112.1. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=96.4 (C), 118.1 (d, $J_{F,C}$=22.5 Hz, CH), 122.2 (d, $J_{F,C}$=3.2 Hz, C), 124.2 (C), 128.5, 129.1, 129.6 (CH), 131.4 (d, $J_{F,C}$=10.0 Hz, CH), 141.3, 144.2 (C), 165.4 (d, $J_{F,C}$=244.7 Hz, C). IR (KBr): ν=3033, 3001, 2951, 2901, 2855 (w), 1730 (w), 1607, 1543 (m), 1482, 1357, 1229 (s), 1149, 990 (m), 849 (s), 826, 731, 609, 585 (m) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%)=408 ([M, $^{79}Br_2]^+$, 100), 174 (13), 136 (12), 131 (10). HRMS (ESI^+): calcd for $C_{16}H_{12}Br_2FN_2$ ($[M+H]^+$, $^{79}Br_2$): 408.8012; found 408.8013.

*3.1.14. 1-Benzyl-3,4-dibromo-5-(4-methoxyphenyl)-1H-pyrazole (**4n**).* Starting with **2c** (197 mg, 0.50 mmol), $Pd(PPh_3)_2Cl_2$ (10 mg, 3 mol %), K_2CO_3 (H_2O, 2 M, 0.5 mL) and 4-methoxyphenylboronic acid (83 mg, 0.55 mmol), **4n** was isolated as a white solid (161 mg, 76%). Mp=84 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=3.75 (s, 3H, OCH_3), 5.12 (s, 2H, CH_2), 6.86 (d, *J*=7.1 Hz, 2H, ArH), 6.94 (d, *J*=7.0 Hz, ArH), 7.09–7.20 (m, 5H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=54.5 (CH_2), 55.3 (OCH_3), 97.0 (C), 114.3 (CH), 120.0 (C), 127.1 (CH), 127.8 (C), 127.9, 128.7, 131.1 (CH), 136.3, 143.5, 160.6 (C). IR (KBr): ν=3031, 3002, 2957, 2917, 2833 (w), 1608, 1540, 1482, 1447, 1367, 1357 (m), 1248, 1174 (s), 1029, 998 (s), 833 (m), 726 (s), 562 (m) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%)=420 ([M, $^{79}Br_2]^+$, 45), 234 (10), 143 (11), 91 (100), 65 (11). HRMS (ESI^+): calcd for $C_{17}H_{15}Br_2N_2O$ ($[M+H]^+$, $^{79}Br_2$): 420.9546; found 420.9543.

*3.1.15. 4-Bromo-3,5-bis(4-methoxyphenyl)-1-methyl-1H-pyrazole (**5a**).* Starting with **2a** (159 mg, 0.50 mmol), $Pd(PPh_3)_2Cl_2$ (17 mg, **5** mol %), K_2CO_3 (H_2O, 2 M, 0.5 mL) and 4-methoxyphenylboronic acid (167 mg, 1.1 mmol), **5a** was isolated as a white solid (112 mg, 60%). Mp=91–92 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=3.76, 3.83, 3.87 (CH_3), 6.87 (d, *J*=8.4 Hz, 2H, CH), 6.90 (d, *J*=8.1 Hz, 2H, CH), 7.29 (d, *J*=8.6 Hz, 2H, CH), 7.71 (d, *J*=8.3 Hz, 2H, CH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=38.8 (*N*CH_3), 55.2, 55.3 (OCH_3), 93.6 (C), 101.6 (CH_2), 113.8, 113.9 (CH), 115.6, 121.5, 123.3, 124.9 (C), 128.6, 130.6 (CH), 147.9, 158.2, 158.7 (C). IR (KBr): ν=3002, 2923, 2831(w), 1613, 1550, 1494, 1437, 1362, 1290 (m), 1248, 1177 (s), 1028, 1029, 975, 755, 742, 685, 605, 578 (m) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%)=374 ([M, $^{81}Br]^+$, 100), 372 ([M, $^{79}Br]^+$, 51), 265 (15), 107 (07), 281 (13), 207 (100). HRMS (ESI^+): calcd for [M+H, $^{79}Br]^+$: 372.13462; found 385.13464.

*3.1.16. 4-Bromo-3,5-bis(3,5-dimethylphenyl)-1-vinyl-1H-pyrazole (**5b**).* Starting with **2b** (165 mg, 0.50 mmol), $Pd(PPh_3)_2Cl_2$ (17 mg, 5 mol %), K_2CO_3 (H_2O, 2 M, 0.5 mL) and 2,6-dimethylphenylboronic acid (165 mg, 1.1 mmol), **5b** was isolated as a white solid (118 mg, 62%). Mp=89 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=2.31 (s, 6H, $2CH_3$), 2.32 (s, 6H, $2CH_3$), 4.74 (d, 1H, *J*=9.1 Hz, vinyl), 5.78 (d, 1H, *J*=15.3 Hz, vinyl), 6.79 (dd, 1H, *J*=9.1, 15.3 Hz, vinyl CH), 6.90–6.93 (m, 2H, ArH), 6.91–7.06 (m, 4H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=21.3, 21.4 (CH_3), 94.3 (C), 101.6 (CH_2), 125.9 (CH), 126.1, 127.6 (C), 127.7, 128.1, 129.8, 130.3 (CH), 131.6, 138.6, 142.6, 149.8 (C). IR (KBr): ν=3080, 2992, 2824, 1729 (w), 1618 (m), 1575 (w), 1489 (s), 1446 (m), 1205 (m), 1240, 1174 (s), 1151, 1109 (m), 1019 (s), 965 (s), 933 (m), 844 (s), 775 (w), 625 (w), 518 (m) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%)=380 (M, ^{79}Br, 100]), 275 (17), 105 (13), 135 (4). HRMS (ESI^+): calcd for $C_{21}H_{22}N_2Br$ [M+H, $^{79}Br]^+$: 380.94368; found 380.94367.

*3.1.17. 4-Bromo-3,5-bis(4-methoxyphenyl)-1-vinyl-1H-pyrazole (**5c**).* Starting with **2b** (165 mg, 0.5 mmol), $Pd(PPh_3)_2Cl_2$ (17 mg, 5 mol %), K_2CO_3 (H_2O, 2 M, 1 mL) and 4-methoxyphenylboronic acid (167 mg, 1.1 mmol), **5c** was isolated as a white solid (116 mg, 60%). Mp=86 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=3.79 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 4.75 (d, 1H, *J*=8.5 Hz, vinyl), 5.75 (d, 1H, *J*=15.4 Hz, vinyl), 6.78 (dd, 1H, *J*=8.8, 15.3 Hz, vinyl CH), 6.92 (d, 2H, *J*=8.9 Hz, ArH), 6.96 (d, 2H, *J*=8.8 Hz, ArH), 7.30 (d, 2H, *J*=8.8 Hz, ArH), 7.86 (d, 2H, *J*=8.9 Hz, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=55.3, 55.4 (OCH_3), 94.2 (C), 101.6 (CH_2), 113.7, 114.2 (CH), 120.1, 124.5 (C), 129.4, 130.3, 131.7 (CH), 142.2, 149.3, 159.9, 160.4 (C). IR (KBr): ν=3090, 2996, 2834, 1789 (w), 1638 (m), 1574 (w), 1489 (s), 1436 (m), 1307 (w), 1207 (m), 1250, 1178 (s), 1161, 1111 (m), 1029 (s), 1114 (m), 975 (s), 943 (m), 834 (s), 795 (w), 736 (m), 635 (w), 528 (m) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%)=384 ([M, $^{79}Br]^+$, 100), 365 (08), 332 (07), 281 (13), 207 (100), 175 (9), 135 (4). HRMS (ESI^+): calcd for $C_{19}H_{18}N_2BrO_2$ [M+H, $^{79}Br]^+$: 385.05462; found 385.05434.

*3.1.18. 1-Benzyl-4-bromo-3,5-bis(4-fluorophenyl)-1H-pyrazole (**5e**).* Starting with **2c** (197 mg, 0.5 mmol), $Pd(PPh_3)_2Cl_2$ (17 mg, 5 mol %), K_2CO_3 (H_2O, 2 M, 0.5 mL) and 4-fluorophenylboronic acid (154 mg, 1.1 mmol), **5e** was isolated as a white solid (140 mg, 66%). Mp=102–103 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=5.20 (s, 2H, CH_2), 6.95–6.98 (m, 2H, ArH), 7.03–7.09 (m, 4H, ArH), 7.17–7.23 (m, 5H, ArH), 7.84–7.89 (m, 2H, ArH). ^{19}F NMR (300 MHz, $CDCl_3$): δ=−113.5, −110.8. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=53.9 (CH_2), 114.3 (d, $J_{F,C}$=21.5 Hz, CH), 115.0 (d, $J_{F,C}$=21.8 Hz, CH), 123.7 (CH), 1123.9 (C), 126.8 (CH), 127.5 (d, $J_{F,C}$=8.1 Hz, CH), 128.6 (CH), 126.8 (C), 131.9 (d, $J_{F,C}$=8.4 Hz, CH), 135.6, 141.3, 146.6, 160.3 (C), 163.7 (d, $J_{F,C}$=249.0 Hz, C–F), 164.3 (d, $J_{F,C}$=248.6 Hz, C–F). IR (KBr): ν=3061, 2956, 1900, 1667, 1590 (w), 1486 (s), 1446 (m), 1348 (w), 1222 (s), 1177 (w), 1156 (s), 1012 (m), 948 (w), 840 (s), 787 (m), 722 (s), 650 (m), 575 (w) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%)=424 ($[M]^+$, ^{79}Br, 49), 329 (11), 225 (38), 91 (100). HRMS (EI, 70 eV): calcd for $C_{22}H_{15}N_2BrF_2$ [M, $^{79}Br]^+$: 424.03812; found 424.037441.

*3.1.19. 1-Methyl-3,4,5-tri-(p-tolyl)-1H-pyrazole (**6a**).* Starting with **2a** (159 mg, 0.5 mmol), $Pd(OAc)_2$ (7 mg, 5 mol %), SPhos (25 mg, 10 mol %), K_2CO_3 (H_2O, 2 M, 1 mL) and *p*-tolylboronic acid (224 mg, 1.65 mmol), **6a** was isolated as a white solid (160 mg, 91%). Mp=147 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=2.20 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 3.76 (s, 3H, *N*CH_3), 6.84 (d, *J*=8.3 Hz, 2H, ArH), 6.89 (d, *J*=8.3 Hz, 2H, ArH), 6.99 (d, *J*=8.3 Hz, 2H, ArH), 7.03 (d, *J*=8.3 Hz, 2H, ArH), 7.09 (d, *J*=7.8 Hz, 2H, ArH), 7.27 (d, *J*=8.1 Hz, 2H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=21.1, 21.2, 21.3 (CH_3), 37.2

(NCH_3), 118.7, 127.3 (C), 127.9, 128.7, 128.9, 129.1 (CH), 129.3 (C), 130.0, 130.2 (CH), 130.7, 135.6, 136.8, 138.2, 142.1, 148.4 (C). IR (KBr): ν=3018, 2919, 2872 (w), 1579, 1523, 1440, 1315, 1277, 1182, 1112, 1005, 975 (m), 818 (s), 750, 723, 657, 613 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=352 ($[M]^+$, 100), 351 (36). HRMS (ESI^+): calcd for $C_{25}H_{25}N_2$ $[M+H]^+$: 353.2012; found 353.2012.

*3.1.20. 3,4,5-Tris(4-ethylphenyl)-1-methyl-1H-pyrazole (**6b**).* Starting with **2a** (159 mg, 0.5 mmol), $Pd(OAc)_2$ (7 mg, 5 mol %), SPhos (25 mg, 10 mol %), K_2CO_3 (H_2O, 2 M, 1 mL) and 4-ethylphenylboronic acid (247 mg, 1.65 mmol), **6b** was isolated as a white solid (175 mg, 89%). Mp=134 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=1.09–1.20 (m, 9H, $3CH_3$), 2.46–2.63 (m, 6H, $3CH_2$), 3.76 (s, 3H, NCH_3), 6.89 (d, J=8.2 Hz, 2H, ArH), 6.92 (d, J=8.4 Hz, 2H, ArH), 7.02 (d, J=8.0 Hz, 2H, ArH), 7.06 (d, J=8.3 Hz, 2H, ArH), 7.10 (d, J=8.7 Hz, 2H, ArH), 7.30 (d, J=8.2 Hz, 2H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=14.1, 14.2, 14.3 (CH_3), 27.3, 27.5, 27.6 (CH_2), 36.2 (NCH_3), 117.6 (C), 126.4, 126.5 (CH), 126.6 (C), 126.8, 126.9, 129.0, 129.2 (CH), 129.7, 130.0, 140.8, 141.1, 142.0, 143.3, 147.4 (C). IR (KBr): ν=3019, 2961, 2871 (w), 1573, 1521, 1440, 1358, 1260, 1114, 1047, 1006, 976 (m), 833 (s), 753, 657, 615 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=394 ($[M]^+$, 100), 379 (29). HRMS (ESI^+): calcd for $C_{28}H_{31}N_2$ (M+H): 395.2482; found 395.24.86.

*3.1.21. 3,4,5-Tris(4-tert-butylphenyl)-1-methyl-1H-pyrazole (**6c**).* Starting with **2a** (159 mg, 0.5 mmol), $Pd(OAc)_2$ (7 mg, 5 mol %), SPhos (25 mg, 10 mol %), K_2CO_3 (H_2O, 2 M, 1 mL) and 4-*tert*-butylphenylboronic acid (293 mg, 1.65 mmol), **6c** was isolated as a white solid (205 mg, 86%). Mp=123 °C. ^1H NMR (250 MHz, $CDCl_3$): δ=1.20 (s, 9H, $3CH_3$), 1.22 (s, 9H, $3CH_3$), 1.25 (s, 9H, $3CH_3$), 3.75 (s, 3H, NCH_3), 6.93 (d, J=8.4 Hz, 2H, ArH), 7.08 (d, J=8.5 Hz, 2H, ArH), 7.10 (d, J=7.3 Hz, 2H, ArH), 7.18 (d, J=8.2 Hz, 2H, ArH), 7.28 (d, J=8.2 Hz, 2H, ArH), 7.33 (d, J=8.5 Hz, 2H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=31.2, 31.3, 31.4 (CH_3), 37.3 (NCH_3), 118.6 (C), 124.8, 125.0, 125.2 (CH), 126.2 (C), 127.5, 129.8, 130.0 (CH), 130.4, 130.8, 142.1, 148.3, 148.8, 149.9, 151.2 (C). IR (KBr): ν=3029, 2959, 2867 (w), 1525, 1436, 1362, 1264, 1201, 1128, 1016, 975 (m), 838 (s), 799, 727, 656, 550 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=478 ($[M]^+$, 96), 464 (37), 463 (100), 224 (14). HRMS (ESI, 70 eV): calcd for $C_{34}H_{42}N_2$ (M+H): 478.33425; found 478.334253.

*3.1.22. 3,4,5-Tris(3,5-dimethylphenyl)-1-methyl-1H-pyrazole (**6d**).* Starting with **2a** (159 mg, 0.5 mmol), $Pd(OAc)_2$ (7 mg, 5 mol %), SPhos (25 mg, 10 mol %), K_2CO_3 (H_2O, 2 M, 1 mL) and 3,5-dimethylphenylboronic acid (247 mg, 1.65 mmol), **6d** was isolated as a white solid (165 mg, 84%). Mp=167 °C. ^1H NMR (250 MHz, $CDCl_3$): δ=2.06 (s, 6H, $2CH_3$), 2.14 (s, 6H, $2CH_3$), 2.20 (s, 6H, $2CH_3$), 3.74 (s, 3H, NCH_3), 6.61 (s, 2H, ArH), 6.69 (s, 1H, ArH), 6.74 (s, 1H, ArH), 6.79 (s, 2H, ArH), 6.89 (s, 1H, ArH), 7.04 (s, 2H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=21.1, 21.2, 21.3 ($6CH_3$), 37.3 (NCH_3), 123.3 (C), 125.8, 127.8, 127.9, 128.2, 128.8, 130.0 (CH), 130.2, 133.2, 133.4, 136.9, 137.3, 138.0, 142.3, 148.3 (C). IR (KBr): ν=3003, 2915, 2857, 1738 (w), 1600 (s), 1444, 1358, 1261, 1152, 1036, 912 (m), 848 (s), 789, 733, 694, 651 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=394 ($[M]^+$, 100), 393 (26). HRMS (ESI^+): calcd for $C_{28}H_{31}N_2$ (M+H): 395.2482; found 395.2483.

*3.1.23. 3,4,5-Tris(4-fluorophenyl)-1-methyl-1H-pyrazole (**6e**).* Starting with **2a** (159 mg, 0.5 mmol), $Pd(OAc)_2$ (7 mg, 5 mol %), SPhos (25 mg, 10 mol %), K_2CO_3 (H_2O, 2 M, 1 mL) and 4-fluorophenylboronic acid (231 mg, 1.65 mmol), **6e** was isolated as a white solid (158 mg, 87%). Mp=121 °C. ^1H NMR (250 MHz, $CDCl_3$): δ=3.76 (s, 3H, NCH_3), 6.81 (d, J=8.6 Hz, 2H, ArH), 6.87 (d, J=7.8 Hz, 2H, ArH), 6.92 (d, J=8.7 Hz, 2H, ArH), 7.00 (d, J=8.5 Hz, 2H, ArH), 7.13 (d, J=8.6 Hz, 2H, ArH), 7.33 (d, J=8.7 Hz, 2H, ArH). ^{19}F NMR (282 MHz, $CDCl_3$): δ=−111.9, −114.5, −115.5. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=37.3 (NCH_3), 115.2 (d, $J_{F,C}$=21.4 Hz, CH), 115.4 (d, $J_{F,C}$=21.4 Hz, CH), 115.8 (d, $J_{F,C}$=21.6 Hz, CH), 118.1 (C), 125.7 (d, $J_{F,C}$=3.6 Hz, C), 129.0 (d, $J_{F,C}$=3.2 Hz, C), 129.2 (d, $J_{F,C}$=3.2 Hz, C), 129.6 (d, $J_{F,C}$=8.1 Hz, CH), 131.8 (d, $J_{F,C}$=8.0 Hz, CH), 131.9 (d, $J_{F,C}$=8.1 Hz, CH), 159.7, 160.3, 160.8, 163.6, 164.3, 164.7 (C). IR (KBr): ν=3003, 2915, 2857, 1738 (w), 1600 (s), 1444, 1358, 1261, 1152, 1036, 912 (m), 848 (s), 789, 733, 694, 651 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=364($[M]^+$, 100), 393 (26). HRMS (ESI^+): calcd for $C_{22}H_{16}F_3N_2$ (M+H): 365.126; found 365.1263.

*3.1.24. 3,4,5-Tris(4-methoxyphenyl)-1-methyl-1H-pyrazole (**6f**).* Starting with **2a** (159 mg, 0.5 mmol), $Pd(OAc)_2$ (7 mg, 5 mol %), SPhos (25 mg, 10 mol %), K_2CO_3 (H_2O, 2 M, 1 mL) and 4-methoxyphenylboronic acid (251 mg, 1.65 mmol), **6f** was isolated as a white solid (162 mg, 81%). Mp=161 °C. ^1H NMR (250 MHz, $CDCl_3$): δ=3.66 (s, 3H, CH_3), 3.69 (s, 3H, CH_3), 3.71 (s, 3H, CH_3), 3.74 (s, 3H, CH_3), 6.63 (d, J=8.8 Hz, 2H, ArH), 6.72 (d, J=8.8 Hz, 2H, ArH), 6.79 (d, J=8.8 Hz, 2H, ArH), 6.88 (d, J=8.8 Hz, 2H, ArH), 7.06 (d, J=8.5 Hz, 2H, ArH), 7.31 (d, J=8.5 Hz, 2H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=37.2 (NCH_3), 55.0 (OCH_3), 55.1 (OCH_3), 55.2 (OCH_3), 113.6, 113.7, 113.9 (CH), 118.1, 122.5, 126.0, 126.3, 126.7 (C), 129.2, 131.4, 131.5 (CH), 141.8, 148.1, 158.0, 158.8, 159.9 (C). IR (KBr): ν=3019, 2961, 2871 (w), 1573, 1521, 1440, 1358, 1260, 1114, 1047, 1006, 976 (m), 833 (s), 753, 657, 615 cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=400 ($[M]^+$, 100), 399 (13), 385 (20). HRMS (ESI, 70 eV): calcd for $C_{25}H_{25}N_2O_3$ (M+H): 401.186; found 401.1868.

*3.1.25. 3,4,5-Tris(4-ethylphenyl)-1-vinyl-1H-pyrazole (**6g**).* Starting with **2b** (165 mg, 0.5 mmol), $Pd(OAc)_2$ (7 mg, 5 mol %), SPhos (25 mg, 10 mol %), K_2CO_3 (H_2O, 2 M, 1 mL) and 4-ethylphenylboronic acid (247 mg, 1.65 mmol), **6g** was isolated as a white solid (134 mg, 66%). Mp=133 °C. ^1H NMR (250 MHz, $CDCl_3$): δ=1.08–1.19 (m, 9H, $3CH_3$), 2.44–2.61 (m, 6H, $3CH_2$), 4.71 (d, 1H, J=8.0 Hz, vinyl), 5.76 (d, 1H, J=15.1 Hz, vinyl), 6.82 (d, J=15.2 Hz, vinyl), 6.87 (d, J=8.4 Hz, 2H, ArH), 6.91 (d, J=8.3 Hz, 2H, ArH), 7.01 (d, J=8.1 Hz, 2H, ArH), 7.04 (d, J=8.4 Hz, 2H, ArH), 7.06 (d, J=8.4 Hz, 2H, ArH), 7.27 (d, J=7.9 Hz, 2H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=14.3, 14.4, 14.5 (CH_3), 27.1, 27.2, 27.3 (CH_2), 118.3 (C), 126.9 (C), 127.2, 127.4, 127.7, 127.9, 129.3, 129.5 (CH), 129.9, 130.2, 140.9, 141.3, 142.2, 143.5, 147.7 (C). IR (KBr): ν=3023, 2951, 2861 (w), 1572, 1520, 1443, 1359, 1262, 1116, 1049, 976 (m), 832 (s), 753, 657 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=406 ($[M]^+$, 100), 259 (14), 196 (12), 105 (14). HRMS (EI, 70 eV): calcd for $C_{29}H_{30}N_2$ $[M]^+$: 406.14080; found: 406.140571.

*3.1.26. 3,4,5-Tris(4-tert-butylphenyl)-1-vinyl-1H-pyrazole (**6h**).* Starting with **2b** (165 mg, 0.5 mmol), $Pd(OAc)_2$ (7 mg, 5 mol %), SPhos (25 mg, 10 mol %), K_2CO_3 (H_2O, 2 M, 1 mL) and 4-*tert*-butylphenylboronic acid (293 mg, 1.65 mmol), **6h** was isolated as a white solid (178 mg, 73%). Mp=129 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=1.21 (s, 9H, $3CH_3$), 1.23 (s, 9H, $3CH_3$), 1.25 (s, 9H, $3CH_3$), 4.70 (d, 1H, J=8.7 Hz, vinyl), 5.79 (d, 1H, J=15.3 Hz, vinyl), 6.84 (d, J=15.3 Hz, vinyl), 6.92–6.95 (m, 2H, ArH), 7.10–7.13 (m, 2H, ArH), 7.18–7.22 (m, 4H, ArH), 7.27–7.30 (m, 2H, ArH), 7.37–7.39 (m, 2H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=31.1, 31.2, 31.3 (CH_3), 34.4, 34.5, 34.6 (C), 100.3 (CH_2), 120.5 (C), 124.5, 124.8, 125.5 (CH), 126.2, 126.6 (C), 127.7 (CH), 128.1, 129.8 (CH), 129.9 (C), 130.0 (CH), 130.3, 133.3, 135.7, 146, 152.2 (C). IR (KBr): ν=3014, 2905, 2852 (w), 1640 (m), 1600 (s), 1540 (w), 1442 (m), 1363 (s), 1238 (s), 1203, 1154, 1110, 1090 (m), 996, 900, 883 (w), 847 (s), 788 (w), 690 (m), 541 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=490 ($[M]^+$, 100), 433 (26), 357 (10). HRMS (EI, 70 eV): calcd for $C_{35}H_{42}N_2$ $[M]^+$: 490.53480; found: 490.534711.

*3.1.27. 3,4,5-Tris(3,5-dimethylphenyl)-1-vinyl-1H-pyrazole (**6i**).* Starting with **2b** (165 mg, 0.5 mmol), $Pd(OAc)_2$ (7 mg,

5 mol %), SPhos (25 mg, 10 mol %), K_2CO_3 (H_2O, 2 M, 1 mL) and 3, 5-dimethylphenylboronic acid (247 mg, 1.65 mmol), **6i** was isolated as a white solid (144 mg, 71%). Mp=128–129 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.06 (s, 6H, $2CH_3$), 2.10 (s, 6H, $2CH_3$), 2.15 (s, 6H, $2CH_3$), 4.69 (d, 1H, J=8.7 Hz, vinyl), 5.78 (d, 1H, J=15.3 Hz, vinyl), 6.61–6.90 (m, 8H), 7.09 (br s, 2H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=21.1, 21.2, 21.3 (CH_3), 100.5 (CH_2), 120.5 (C), 126.2, 128.1, 128.2, 128.5 (CH), 129.2 (C), 129.3, 130.3, 130.4 (CH), 132.6, 133.0, 137.0, 137.4, 137.8, 141.8, 150.4 (C). IR (KBr): ν=3002, 2915, 2859 (w), 1738, 1642 (m), 1600 (s), 1550 (w), 1444 (m), 1373 (s), 1303, 1268 (w), 1237 (s), 1203, 1154, 1110, 1096 (w), 1093 (m), 996, 900, 881 (w), 848 (s), 789 (w), 691 (m), 542 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=406 ([M]$^+$, 100), 391 (26), 375 (02), 259 (04), 203 (03), 180 (02), 132 (04). HRMS (EI, 70 eV): calcd for $C_{29}H_{30}N_2$ [M]$^+$: 406.24090; found: 406.240571.

*3.1.28. 1-Benzyl-3,4,5-tris(4-chlorophenyl)-1H-pyrazole (**6j**).* Starting with **2c** (197 mg, 0.5 mmol), $Pd(OAc)_2$ (7 mg, 5 mol %), SPhos (25 mg, 10 mol %), K_2CO_3 (H_2O, 2 M, 1 mL) and 4-chlorophenylboronic acid (257 mg, 1.65 mmol), **6j** was isolated as a white solid (186 mg, 76%). Mp=167 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=5.20 (s, 2H, CH_2), 684–6.87 (m, 2H, ArH), 6.92–6.95 (m, 2H, ArH), 7.00–7.08 (m, 4H, ArH), 7.17–7.22 (m, 7H, ArH), 7.31–7.34 (m, 2H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=53.2 (CH_2), 127.1, 127.7 (CH), 128.0 (C), 128.6, 128.8, 128.9, 129.0, 129.5 (CH), 130.9, 131.2, 131.4 (C), 131.5, 131.9 (CH), 132.7, 133.6, 135.1, 136.9, 141.4, 147.8 (C). IR (KBr): ν=3089, 3031, 1913, 1601, 1496 (w), 1441 (m), 1391, 1268 (w), 1152 (m), 1089 (s), 1031 (w), 1008, 980 (s), 956 (w), 841 (s), 784 (w), 734 (s), 609 (w), 542 (s) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=488 ([M, $^{35}Cl_3$]$^+$, 100), 343 (13), 327 (22), 277 (39), 246 (22), 198 (23). HRMS (EI, 70 eV): calcd for $C_{28}H_{19}N_2Cl_3$ [M, $^{35}Cl_3$]$^+$: 488.91544; found 488.915354.

*3.1.29. 1-Benzyl-3,4,5-tris(4-fluorophenyl)-1H-pyrazole (**6k**).* Starting with **2c** (197 mg, 0.62 mmol), $Pd(OAc)_2$ (7 mg, 5 mol %), SPhos (25 mg, 10 mol %), K_2CO_3 (H_2O, 2 M, 1 mL) and 4-fluorophenylboronic acid (231 mg, 1.65 mmol), **6k** was isolated as a white solid (171 mg, 78%). Mp=151 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ=5.21 (s, 2H, CH_2), 6.76–6.81 (m, 2H, ArH), 6.87–6.90 (m, 3H, ArH), 6.92–6.94 (m, 2H, ArH), 6.97–7.03 (m, 4H, ArH), 7.18–7.22 (m, 4H, ArH), 7.34–7.39 (m, 2H, ArH). ^{19}F NMR (282 MHz, $CDCl_3$): δ=−111.8, −114.5, −115.6. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=53.5 (CH_2), 115.2 (d, $J_{F,C}$=21.2 Hz, CH), 115.3 (d, $J_{F,C}$=21.3 Hz, CH), 115.8 (d, $J_{F,C}$=22.9 Hz, CH), 118.5 (C), 127.0, 127.6, 128.6 (CH), 128.8, 128.9, 129.4 (C), 129.8 (d, $J_{F,C}$=7.9 Hz, CH), 131.8 (d, $J_{F,C}$=8.0 Hz, CH), 132.1 (d, $J_{F,C}$=7.9 Hz, CH), 137.1, 141.4, 147.9, 159.7, 160.4, 164.8 (C). IR (KBr): ν=3063, 2953, 2924, 2851 (w), 1604, 1593, 1491, 1443 (m), 1223, 1156 (s), 1094, 975, 908 (m), 838, 816 (s), 720, 601, 530 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=440 ([M]$^+$, 100), 345 (15), 321 (11), 91 (48). HRMS (ESI$^+$): calcd for $C_{28}H_{19}N_2$ (M+H): 441.126; found 441.1263.

*3.1.30. 1-Benzyl-3,4,5-tri-p-tolyl-1H-pyrazole (**6l**).* Starting with **2c** (197 mg, 0.5 mmol), $Pd(OAc)_2$ (7 mg, 5 mol %), SPhos (25 mg, 10 mol %), K_2CO_3 (H_2O, 2 M, 1 mL) and 4-methylphenylboronic acid (224 mg, 1.65 mmol), **6l** was isolated as a white solid (173 mg, 81%). Mp=174 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.18 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 5.20 (s, 2H, CH_2), 6.84–6.87 (m, 4H, ArH), 6.91–6.94 (m, 2H, ArH), 6.98–7.02 (m, 2H, ArH), 7.03–7.05 (m, 2H, ArH), 7.16–7.19 (m, 3H, $3CH_3$). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=21.1, 21.2, 21.3 (CH_3), 53.1 (CH_2), 115.1, 119.0 (C), 127.1 (CH), 127.3 (C), 128.1, 128.4, 128.7, 128.8, 129.1 (CH), 129.9 (C), 130.1, 130.2 (CH), 130.4, 130.8, 135.6, 136.9, 137.7, 138.2, 142.4, 148.9 (C). IR (KBr): ν=3065, 3018, 2918, 2862 (w), 1494, 1452 (s), 1361 (m), 1309, 1294, 1185, 1113, 1028, 973, 852, 829 (m), 815, 733, 721 (m), 693 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=428 ([M]$^+$, 100), 427(57), 337 (15), 309 (18), 91 (16). HRMS (EI, 70 eV): calcd for $C_{31}H_{28}N_2$ [M]$^+$: 428.22470; found 428.224038.

*3.1.31. 1-Benzyl-3,4,5-tris(4-ethylphenyl)-1H-pyrazole (**6m**).* Starting with **2c** (197 mg, 0.5 mmol), $Pd(OAc)_2$ (7 mg, 5 mol %), SPhos (25 mg, 10 mol %), K_2CO_3 (H_2O, 2 M, 1 mL) and 4-ethylphenylboronic acid (247 mg, 1.65 mmol), **6m** was isolated as a white solid (197 mg, 84%). Mp=169 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.08–1.17 (m, 9H, $3CH_3$), 2.46–2.58 (m, 6H, $3CH_2$), 5.20 (s, 2H, CH_2), 689–7.05 (m, 12H, ArH), 7.13–7.19 (m, 3H, ArH), 7.33–7.36 (m, 2H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=15.1, 15.2, 15.4 (CH_3), 28.4, 28.5, 28.6, 53.2 (CH_2), 127.1, 127.3, 127.4 (CH), 127.5(C), 127.6(CH), 127.8(C), 128.1, 128.4, 130.2, 130.3 (CH), 130.7, 131.1, 137.8, 141.8, 142.4, 143.1, 144.4, 148.9 (C). IR (KBr): ν=3063 (w), 2962 (m), 2871, 1910, 1524 (w), 1494, 1452 (s), 1373 (m), 1253, 1155, 1062, 981 (w), 957 (m), 837 (s), 792 (m), 724, 694 (s), 595, 536 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=470 ([M]$^+$, 02), 446 (16), 366 (100), 351 (08), 289 (12), 261 (12). HRMS (EI, 70 eV): calcd for $C_{34}H_{34}N_2$ [M]$^+$: 470.27215; found 470.27208.

*3.1.32. 1-Methyl-3,4-diphenyl-5-p-tolyl-1H-pyrazole (**7a**).* Starting with **4a** (100 mg, 0.30 mmol), $Pd(OAc)_2$ (7 mg, 5 mol %), SPhos (25 mg, 10 mol %), K_2CO_3 (H_2O, 2 M, 0.5 mL) and phenylboronic acid (80 mg, 0.66 mmol), **7a** was isolated as a white solid (89 mg, 92%). Mp=147 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.28 (s, 3H, CH_3), 3.78 (s, 3H, NCH_3), 6.95–6.98 (m, 2H, ArH), 7.03–7.05 (m, 1H, ArH), 7.07–7.10 (m, 4H, ArH), 7.06–7.09 (m, 2H, ArH), 7.15–7.22 (m, 4H, ArH), 7.37–7.40 (m, 1H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=21.3, 37.3 (NCH_3), 118.9 (C), 126.2, 128.0, 129.2, 130.0, 130.4 (CH), 122.5 (C), 127.9, 128.8, 128.9, 130.2 (CH), 130.4, 133.4, 138.3, 142.3, 148.4 (C). IR (KBr): ν=3051, 2921, 2850 (w), 1600, 1519 (w), 1483, 1356, 1232, 1006, 831 (m), 760, 694 (s), 626, 566 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=324 ([M]$^+$, 100), 323 (53). HRMS (ESI$^+$): calcd for $C_{23}H_{21}N_2$ ([M+H]$^+$): 325.1699; found 325.1703.

*3.1.33. 3,4-Bis(4-methoxyphenyl)-1-methyl-5-p-tolyl-1H-pyrazole (**7b**).* Starting with **4a** (100 mg, 0.30 mmol), $Pd(OAc)_2$ (7 mg, 5 mol %), SPhos (25 mg, 10 mol %), K_2CO_3 (H_2O, 2 M, 0.5 mL) and 4-methoxyphenylboronic acid (100 mg, 0.66 mmol), **7b** was isolated as a white solid (97 mg, 84%). Mp=159–160 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.28 (s, 3H, CH_3), 3.68 (s, 3H, CH_3), 3.71 (s, 3H, CH_3), 3.76 (s, 3H, CH_3), 6.63–6.66 (m, 3H, ArH), 6.72–6.75 (m, 3H, ArH), 6.87–6.90 (m, 3H, ArH), 7.02–7.10 (m, 5H, ArH), 7.30–7.33 (m, 2H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=21.3 (CH_3), 37.2 (NCH_3), 55.0, 55.1 (OCH_3), 113.5, 113.6 (CH), 118.1, 125.9, 126.2, 127.3 (C), 129.1, 129.2, 130.0, 131.4 (CH), 138.1, 142.0, 148.1, 157.9, 158.8 (C). IR (KBr): ν=3011, 2923, 2832, 1611 (w), 1520, 1432, 1283 (m), 1241 (s), 1172 (s), 1033, 837, 807 (m), 755, 612, 530 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=384 ([M]$^+$, 100), 341 (13), 327 (22), 277 (39), 246 (22), 198 (23). HRMS (ESI$^+$): calcd for $C_{25}H_{25}N_2O_2$ [M+H]: 385.1911; found 385.1914.

*3.1.34. 5-(4-Ethylphenyl)-1-methyl-3,4-diphenyl-1H-pyrazole (**7c**).* Starting with **4b** (103 mg, 0.3 mmol), $Pd(OAc)_2$ (7 mg, 5 mol %), SPhos (25 mg, 10 mol %), K_2CO_3 (H_2O, 2 M, 1 mL) and phenylboronic acid (80 mg, 0.66 mmol), **7c** was isolated as a white solid (90 mg, 89%). Mp=153 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.18 (t, J=7.5 Hz, 3H, CH_3), 2.59 (q, J=7.6 Hz, 2H, CH_2), 3.79 (s, 3H, NCH_3), 6.96–6.99 (m, 2H, ArH), 7.05–7.10 (m, 5H, ArH), 7.17–7.21 (m, 5H, ArH), 7.37–7.40 (m, 2H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=15.1 (CH_3), 28.5 (CH_2), 37.3 (NCH_3), 125.5 (C), 126.2, 127.2, 127.9, 128.0, 128.1 (CH), 128.5, 128.7 (C), 130.0, 130.4 (CH), 133.5, 142.3, 144.5, 148.4 (C). IR (KBr): ν=3051, 2959, 2924, 2848, 1603, 1519, 1454, 1361, 1277, 1117, 1058, 1007, 973, 916 (w), 841 (m), 761, 696 (s), 627, 536 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=338 ([M]$^+$, 100),

337 (45). HRMS (EI, 70 eV): calcd for $C_{24}H_{23}N_2$ [M+H]: 339.1856; found 339.1861.

*3.1.35. 3,4-Bis(3-chlorophenyl)-5-(4-ethylphenyl)-1-methyl-1H-pyrazole (**7d**).* Starting with **4b** (103 mg, 0.3 mmol), $Pd(OAc)_2$ (7 mg, 5 mol %), SPhos (25 mg, 10 mol %), K_2CO_3 (H_2O, 2 M, 0.5 mL) and 3-chlorophenylboronic acid (99 mg, 0.66 mmol), **7d** was isolated as a white solid (100 mg, 82%). Mp=148 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.18 (t, J=7.5 Hz, 3H, CH_3), 2.59 (q, J=7.6 Hz, 2H, CH_2), 3.79 (s, 3H, NCH_3), 6.96–6.99 (m, 2H, ArH), 7.05–7.10 (m, 5H, ArH), 7.17–7.21 (m, 3H, ArH), 7.37–7.40 (m, 2H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=15.1 (CH_3), 28.6 (CH_2), 37.4 (NCH_3), 117.8 (C), 126.2 (CH), 126.5 (C), 126.7, 127.3, 127.5, 127.9, 128.1, 128.6 (CH), 128.7 (C), 129.4, 129.9, 130.1 (CH), 133.9, 134.2, 135.1, 142.7, 145.0, 147.0 (C). IR (KBr): ν=3063, 2961, 2872 (w), 1596, 1455, 1409, 1359, 1304, 1257, 1111, 1076, 997, 880, 847 (w), 786, 759, 697 (s), 635, 556 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=406 ([M]$^+$, 100), 405 (26), 391 (10). HRMS (EI, 70 eV): calcd for $C_{24}H_{21}Cl_2N_2$ [M+H]: 407.1076; found 407.1074.

*3.1.36. 5-(4-Ethylphenyl)-3,4-bis(4-methoxyphenyl)-1-methyl-1H-pyrazole (**7e**).* Starting with **4b** (103 mg, 0.3 mmol), $Pd(OAc)_2$ (7 mg, 5 mol %), SPhos (25 mg, 10 mol %), K_2CO_3 (H_2O, 2 M, 0.5 mL) and 4-methoxyphenylboronic acid (100 mg, 0.66 mmol), **7e** was isolated as a white solid (102 mg, 86%). Mp=169 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.17 (t, J=7.5 Hz, 3H, CH_3), 2.58 (q, J=7.6 Hz, 2H, CH_2), 3.68 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 3.76 (s, 3H, NCH_3), 6.64 (d, J=8.8 Hz, 2H, ArH), 6.73 (d, J=9.0 Hz, 2H, ArH), 6.89 (d, J=8.8 Hz, 2H, ArH), 7.07 (d, J=8.2 Hz, 2H, ArH), 7.11 (d, J=8.2 Hz, 2H, ArH), 7.32 (d, J=9.1 Hz, 2H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=15.1 (CH_3), 28.5 (CH_2), 37.2 (NCH_3), 55.0, 55.1 (OCH_3), 113.5, 113.6 (CH), 118.1, 125.9, 126.2, 127.4 (C), 127.9, 129.2, 130.0, 131.4 (CH), 142.1, 144.3, 148.1, 157.9, 158.8 (C). IR (KBr): ν=3010, 2961, 2925, 2832 (w), 1612, 1578, 1547, 1520, 1463, 1433, 1354, 1283 (m), 1242, 1171 (s), 1110, 1034, 973 (m), 833 (s), 809, 756, 608, 544 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=398 ([M]$^+$, 100), 397 (12), 383 (18). HRMS (ESI$^+$): calcd for $C_{26}H_{27}N_2O_2$ [M+H]: 399.2067; found 399.2071.

*3.1.37. 5-(4-Chlorophenyl)-1-methyl-3,4-diphenyl-1H-pyrazole (**7f**).* Starting with **4e** (105 mg, 0.3 mmol), $Pd(OAc)_2$ (7 mg, 5 mol %), SPhos (25 mg, 10 mol %), K_2CO_3 (H_2O, 2 M, 0.5 mL) and phenylboronic acid (80 mg, 0.66 mmol), **7f** was isolated as a white solid (82 mg, 79%). Mp=157 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.85 (s, 3H, NCH_3), 6.99–7.02 (m, 2H, ArH), 7.09–7.12 (m, 2H, ArH), 7.22–7.25 (m, 3H, ArH), 7.28–7.34 (m, 2H, ArH), 7.38–7.42 (m, 3H, ArH), 7.50–7.54 (m, 2H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=37.5 (NCH_3), 119.2 (C), 127.0 (CH), 127.1 (C), 127.2, 128.1, 128.2, 128.3, 128.8, 130.4, 130.5 (CH), 133.4, 133.5, 140.2, 141.1, 141.9, 148.5 (C). IR (KBr): ν=3011, 2923, 2832, 1611 (w), 1520, 1432, 1283 (m), 1241 (s), 1172 (s), 1033, 837, 807 (m), 755, 612, 530 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=346 ([M, ^{37}Cl]$^+$, 100), 344 ([M, ^{35}Cl]$^+$, 99). HRMS (EI, 70 eV): calcd for ([M$^+$, [^{35}Cl]): 344.91324; found 344.9133.

*3.1.38. 5-(4-Chlorophenyl)-3,4-bis(4-ethylphenyl)-1-methyl-1H-pyrazole (**7g**).* Starting with **4e** (105 mg, 0.3 mmol), $Pd(OAc)_2$ (7 mg, 5 mol %), SPhos (25 mg, 10 mol %), K_2CO_3 (H_2O, 2 M, 0.5 mL) and 4-ethylboronic acid (99 mg, 0.66 mmol), **7g** was isolated as a white solid (97 mg, 81%). Mp=149 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.12–1.17 (m, 6H, $2CH_3$), 2.49–2.59 (m, 4H, ArH), 3.75 (s, 3H, CH_3), 6.86 (d, J=8.0 Hz, 2H, ArH), 6.93 (d, J=7.3 Hz, 2H, ArH), 7.02 (d, J=8.0 Hz, 2H, ArH), 7.09 (d, J=8.1 Hz, 2H, ArH), 7.26 (d, J=8.3 Hz, 2H, ArH), 7.30 (d, J=8.0 Hz, 2H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=14.1, 14.3 (CH_3), 28.4, 28.5 (CH_2), 36.3 (NCH_3), 118.1, 125.9 (C), 126.9 (CH), 127.3 (C), 127.5, 127.6, 127.9, 128.3, 128.8 (CH), 129.5 (C), 130.2, 131.4 (CH), 133.5, 139.8, 141.2, 142.3, 147.5 (C). IR (KBr): ν=2960, 2913, 2871, 2848 (w), 1525, 1453, 1360, 1259, 1183, 1091, 1007 (m), 835 (s), 755, 675, 628, 604, 538 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=400 ([M, ^{35}Cl]$^+$, 100). HRMS (ESI$^+$): calcd for $C_{26}H_{26}ClN_2$ [M+H]$^+$: 401.1779; found 401.178.

*3.1.39. 5-(4-Methoxyphenyl)-1-methyl-3,4-di-p-tolyl-1H-pyrazole (**7h**).* Starting with **4g** (104 mg, 0.3 mmol), $Pd(OAc)_2$ (7 mg, 5 mol %), SPhos (25 mg, 10 mol %), K_2CO_3 (H_2O, 2 M, 0.5 mL) and *p*-tolylboronic acid (90 mg, 0.66 mmol), **7h** was isolated as a white solid (92 mg, 83%). Mp=157–159 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.20 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 3.73 (s, 3H, CH_3), 3.75 (s, 3H, CH_3), 6.80 (d, J=7.1 Hz, 2H, ArH), 6.84 (d, J=8.3 Hz, 2H, ArH), 6.90 (d, J=8.0 Hz, 2H, ArH), 7.00 (d, J=7.9 Hz, 2H, ArH), 7.08 (d, J=7.0 Hz, 2H, ArH), 7.28 (d, J=8.0 Hz, 2H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=21.1, 21.2 (CH_3), 37.2 (NCH_3), 55.2 (OCH_3), 113.9 (CH), 118.6, 122.5 (C), 127.9, 128.8, 128.9, 130.2 (CH), 130.6, 130.8 (C), 131.4 (CH), 135.6, 136.8, 141.9, 148.4, 159.5 (C). IR (KBr): ν=2951, 2920, 2851 (w), 1612, 1529, 1492, 1353, 1286 (m), 1243, 1178 (s), 1107 (m), 1034 (s), 1020, 845 (m), 824 (s), 800, 755, 721, 614, 530 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=368 ([M]$^+$, 100). HRMS (ESI$^+$): calcd for $C_{25}H_{25}N_2O$ [M+H]$^+$: 369.1961; found 369.1962.

*3.1.40. 3,4-Bis(3-chlorophenyl)-5-(4-methoxyphenyl)-1-methyl-1H-pyrazole (**7i**).* Starting with **4g** (104 mg, 0.3 mmol), $Pd(OAc)_2$ (7 mg, 5 mol %), SPhos (25 mg, 10 mol %), K_2CO_3 (H_2O, 2 M, 0.5 mL) and 3-chlorophenylboronic acid (103 mg, 0.66 mmol), **7i** was isolated as a white solid (102 mg, 83%). Mp=171 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.75 (s, 3H, CH_3), 3.76 (s, 3H, CH_3), 6.81–6.82 (m, 4H, ArH), 6.85 (s, 1H, ArH), 6.94 (s, 1H, ArH), 7.03–7.08 (m, 4H, ArH), 711–7.15 (m, 2H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=37.3 (NCH_3), 55.2 (OCH_3), 114.1 (CH), 117.7, 121.4 (C), 126.2, 126.7, 127.5, 127.9, 128.5, 129.4, 130.0, 130.1, 131.3 (CH), 133.9, 134.2, 135.0, 135.1, 142.4, 146.9, 159.8 (C). IR (KBr): ν=3057, 2926, 2835 (w), 1611, 1597, 1469, 1358, 1290 (m), 1247 (s), 1174, 1077, 1032, 998, 846 (m), 784, 730, 698 (s), 604 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=408 ([M, $^{35}Cl_2$]$^+$, 100). HRMS (ESI$^+$): calcd for $C_{23}H_{19}Cl_2N_2O$ [M+H]$^+$ ($^{35}Cl_2$): 409.0869; found 409.0867.

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