Synthesis of Arylated Pyrazoles by Site-Selective Suzuki–Miyaura Reactions of Tribromopyrazoles

Rasheed Ahmad Khera,[a] Asad Ali,[a] Munawar Hussain,[a] Jovana Tatar,[a] Alexander Villinger,[a] Peter Langer*[a,b]

[a] Institut für Chemie, Universität Rostock, Albert Einstein Str. 3a, 18059 Rostock, Germany
Fax +49(381)4986412; E-mail: peter.langer@uni-rostock.de

[b] Leibniz-Institut für Katalyse an der Universität Rostock e.V., Albert Einstein Str. 29a, 18059 Rostock, Germany

Received 31 March 2010

Abstract: The first Suzuki–Miyaura reactions of N-protected tribromopyrazoles are reported. Their reaction with three, two, or one equivalents of arylboronic acids afforded 3,4,5-triarylpyrazoles, 3,5-diaryl-4-bromopyrazoles, or 5-aryl-3,4-dibromopyrazoles, respectively. All reactions proceeded with very good site-selectivity.

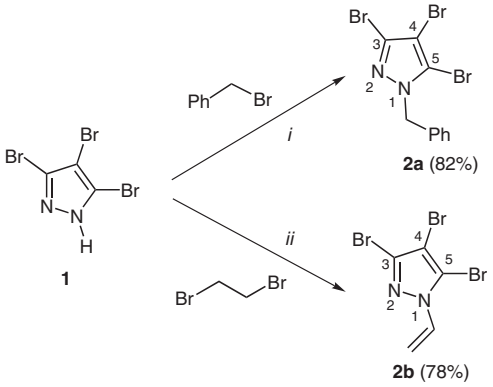
Key words: pyrazoles, catalysis, Suzuki–Miyaura reaction, regioselectivity, palladium

Pyrazoles represent important synthetic building blocks and are important lead structures in medicinal chemistry. Pharmacological properties include activity as nicotinic acid receptor agonists[1a] and excitatory amino acid antagonists, respectively.[1b] Ethyl 5-propyl-1*H*-pyrazole-3-carboxylate is a key intermediate for the synthesis of viagra.[1c] Celecoxib represents a clinically used COX-2 inhibitor which exhibits promising anti-inflammatory and analgesic activity.[1d,e] Nicolaou et al.[1f] reported that a pyrazole-substituted epothilone derivative shows a strong antitumor activity. In fact, it is considered to be the most potent epothilone derivative reported to date.

Pyrazoles are available by cycloaddition of diazoalkanes with alkynes.[2] Other syntheses rely on the cyclization of hydrazines with 1,3-diketones or α,β-unsaturated ketones.[3] An interesting approach to pyrazoles relies on the cyclization of hydrazone dianions, generated by means of *n*-BuLi, with esters, acid chlorides, nitriles, α-haloketones, propiolates, Weinreb amides, and diethyl oxalate.[4] 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.[5]

The development of site-selective cross-coupling reactions of polyhalogenated heterocycles is of considerable current interest.[6,7] Palladium-catalyzed cross-coupling reactions of polyhalogenated pyrazoles have, to the best of our knowledge, not been reported to date. Recently, metal-halide exchange reactions of *N*-vinyl-tribromopyrazole have been reported.[8] Herein, we report our preliminary results related to the first Suzuki–Miyaura reactions of *N*-vinyl- and *N*-benzyltribromopyrazole. The products, triarylpyrazoles, 3,5-diaryl-4-bromopyrazoles, and 5-aryl-3,4-dibromopyrazoles, are of considerable pharmacological relevance.[9] Previous syntheses of these molecules are not straightforward and mainly include derivatives containing one and the same type of aryl moiety.[9]

N-Benzyltribromopyrazole (**2a**) was prepared from commercially available tribromopyrazole by modification of a known procedure (Scheme 1).[10] Instead of benzylchloride, which was used in the original procedure, benzylbromide was employed. *N*-Vinyltribromopyrazole (**2b**) was prepared, following a reported procedure,[8] by reaction of commercially available tribromopyrazole with dibromoethane.

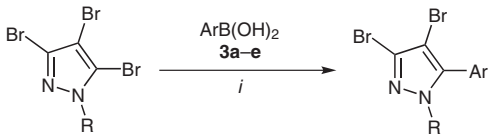


Scheme 1 Synthesis of **2a**,**b**. *Reagents and conditions*: (*i*) **1** (1.0 equiv), benzylbromide (1.0 equiv), Et_3N (1.1 equiv), CH_2Cl_2 (5 mL/mmol of **1**), 20 °C, 4 h; (*ii*) **1** (1.0 equiv), DCE (1.2 equiv), Et_3N (5 mL/mmol), MeCN (5 mL/mmol of **1**), 70 °C, 7 h.

The Suzuki–Miyaura reaction of **2a** and **2b** with arylboronic acids **3a–e** (1.0 equiv) afforded the 5-aryl-3,4-dibromopyrazoles **4a–e** in 66–73% yield (Table 1, Scheme 2).[11,12] A good yield was obtained even for the sterically hindered boronic acid **3d**. During the optimization, the best yields were obtained when $Pd(PPh_3)_4$ was used as the catalyst (3 mol%) and when K_3PO_4 (1.5 equiv) was used as the base. The use of $Pd(OAc)_2$ in the presence of XPhos[13] or of $PdCl_2(PPh_3)_2$ proved to be less efficient in terms of yield. The use of exactly one equivalent of the boronic acid proved to be important to avoid multiple coupling. The reactions were carried out in a 4:1 mixture of dioxane and water. The employment of toluene was less efficient because of the low solubility of the boronic acids. The temperature (100 °C) and the reaction time (12 h) also

SYNLETT 2010, No. 13, pp 1923–1926
Advanced online publication: 09.07.2010
DOI: 10.1055/s-0030-1258489; Art ID: G10210ST

played an important role. The yields decreased when the reaction mixture was stirred for a shorter period of time (no complete conversion) or when the reaction time was extended. The conversion was not complete when the reaction was cariied out at lower temperature. The formation of **4a–e** proceded, like the metal–halide exchange,[8] with excellent site-selectivity in favour of position 5. The configuration of the products was unambiguously confirmed by 2D NMR experiments (NOESY, HMBC, HMQC). 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.



Scheme 2 Synthesis of 5-aryl-3,4-dibromopyrazoles **4a–e**. *Reagents and conditions*: (*i*) **2a**,**b** (1.0 equiv), $ArB(OH)_2$ (1.0 equiv), K_3PO_4 (1.5 equiv), $Pd(PPh_3)_4$ (3 mol%), 1,4-dioxane–H_2O (4:1), 100 °C, 12 h.

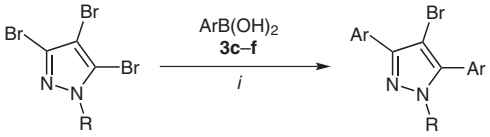
Table 1 Synthesis of **4a–e**

2	3, 4	R	Ar	Yield of **4** (%)[a]
b	**a**	vinyl	4-MeC_6H_4	66
b	**b**	vinyl	2-$MeOC_6H_4$	69
b	**c**	vinyl	4-$MeOC_6H_4$	73
b	**d**	vinyl	2,6-$(MeO)_2C_6H_3$	71
a	**e**	Bn	4-FC_6H_4	68

[a] Yields of isolated compounds.

The Suzuki–Miyaura reaction of **2a** and **2b** with arylboronic acids **3c–f** (2.0 equiv) afforded the 3,5-diaryl-4-bromopyrazoles **5a–d** in 40–74% yield (Table 2, Scheme 3).[11,14] A good yield was obtained even for the sterically hindered boronic acid **3d**. A slightly increased amount of the catalyst (5 mol%), exactly two equivalents of the boronic acid, and the double amount of base (3.0 equiv) were employed. The use of $Pd(OAc)_2$/XPhos or $PdCl_2(PPh_3)_2$ resulted in a decrease of the yield. The yields decreased when the temperature or the reaction time was decreased. Inspection of the crude product mixture showed that a small amount of pyrazole derived from mono and triple Suzuki reaction were formed. The structure of **5a** was independently confirmed by X-ray crystal structure analysis (Figure 1).[15]

The Suzuki–Miyaura reaction of **2a** and **2b** with an excess of arylboronic acids **3a**,**e–j** (3.5 equiv) afforded the 3,4,5-triarylpyrazoles **6a–g** in 50–76% yield (Table 3, Scheme 4).[11,16] During the optimization, it proved to be



Scheme 3 Synthesis of 5-aryl-3,4-dibromopyrazoles **5a–d**. *Reagents and conditions*: (*i*) **2a**,**b** (1.0 equiv), $ArB(OH)_2$ (2.0 equiv), K_3PO_4 (3.0 equiv), $Pd(PPh_3)_4$ (5 mol%), 1,4-dioxane–H_2O (4:1), 100 °C, 12 h.

Table 2 Synthesis of **5a–d**

2	3	5	R	Ar	Yield of **5** (%)[a]
b	**c**	**a**	vinyl	4-$MeOC_6H_4$	60
b	**d**	**b**	vinyl	2,6-$(MeO)_2C_6H_3$	62
b	**f**	**c**	vinyl	3,5-$(MeO)_2C_6H_3$	74
a	**e**	**d**	Bn	4-FC_6H_4	66

[a] Yields of isolated compounds.

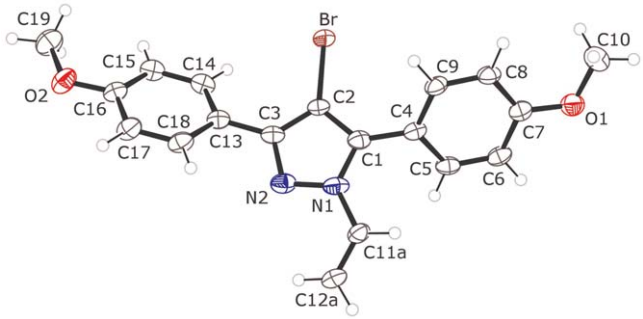
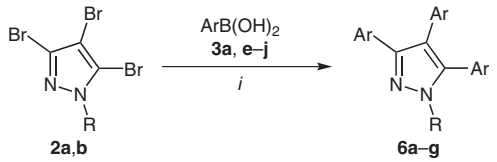


Figure 1 Crystal structure of **5a**

important to use 10 mol% of the catalyst and an excess of the boronic acid (3.5 equiv) and of the base (4.5 equiv). The use of $Pd(OAc)_2$ in the presence of XPhos or of $PdCl_2(PPh_3)_2$ resulted in a decrease of the yield. The best results were again obtained when the reaction was carried out at 100 °C for 12 hours. The yields slightly decreased for products **6b**,**g** derived from the electron-poor boronic acids **3f**,**j**. Inspection of the crude product mixture showed that a small amount of biaryls were formed. It is surprising that the yields of products **6a–g** were in the same range as the yields of products **4a–e** and **5a–d**. This might be explained by increasing steric hindrance during the triple Suzuki reaction, dimerization of the arylboronic acid, and decomposition.

In conclusion, we have reported the first Suzuki–Miyaura reactions of N-protected tribromopyrazoles. Their reaction with three, two, or one equivalents of arylboronic acids afforded triarylpyrazoles, 3,5-diaryl-4-bromopyrazoles, or 5-aryl-3,4-dibromopyrazoles, respectively. The products are not readily available by other methods. All reactions proceed with very good site-selectivity.



Scheme 4 Synthesis of 3,4,5-triarylpyrazoles **6a**–**g**. *Reagents and conditions*: (*i*) **2a**,**b** (1.0 equiv), $ArB(OH)_2$ (3.5 equiv), K_3PO_4 (4.5 equiv), $Pd(PPh_3)_4$ (10 mol%), 1,4-dioxane–H_2O (4:1), 100 °C, 12 h.

Table 3 Synthesis of **6a**–**g**

2	3	6	R	Ar	Yield of **6** (%)[a]
a	**a**	**a**	Bn	4-MeC_6H_4	70
a	**e**	**b**	Bn	4-FC_6H_4	63
b	**f**	**c**	vinyl	3,5-$(MeO)_2C_6H_3$	57
b	**g**	**d**	vinyl	4-*t*-BuC_6H_4	76
b	**h**	**e**	vinyl	4-EtC_6H_4	72
b	**i**	**f**	vinyl	3,5-$Me_2C_6H_3$	74
a	**j**	**g**	Bn	4-ClC_6H_4	50

[a] Yields of isolated compounds.

Acknowledgment

Financial support from the State of Pakistan (HEC scholarship for M.H.), from the DAAD (scholarships for A.A. and R.A.K.), from the State of Mecklenburg-Vorpommern (scholarships for M.H. and J.T.), and from the Friedrich-Irmgard-Harms-Stiftung (scholarship for A.A.) is gratefully acknowledged. Partial financial support by the Ministry of Science of the Republic of Serbia, Grant No. 142007, is gratefully acknowledged.

References and Notes

(1) (a) van Herk, T.; Brussee, J.; van den Nieuwendijk, A. M. C. H.; van der Klein, P. A. M.; Ijzerman, A. P.; Stannek, C.; Burmeister, A.; Lorenzen, A. *J. Med. Chem.* **2003**, *46*, 3945. (b) Varano, F.; Catarzi, D.; Colotta, V.; Filacchioni, G.; Galli, A.; Costagli, C.; Carlà, V. *J. Med. Chem.* **2002**, *45*, 1035. (c) Clayden, J.; Geeves, N.; Warren, S. *Organic Chemistry*; Oxford University Press: Oxford, **2000**. (d) Dannhardt, G.; Laufer, S. *Curr. Med. Chem.* **2000**, 71101. (e) Carty, T. J.; Marfat, A. *Curr. Opin. Anti-Inflamm. Immunomod. Invest. Drugs* **1999**, *1*, 89. (f) Nicolaou, K. C.; Pratt, B. A.; Arseniyadis, S.; Wartmann, M.; O'Brate, A.; Giannakakou, P. *ChemMedChem* **2006**, *1*, 41.

(2) (a) *The Chemistry of Heterocyclic Compounds*, Part 1, Vol. 49; Grunanger, P.; Vita-Finzi, P., Eds.; John Wiley: New York, **1991**. (b) Aggarwal, V. K.; de Vincente, J.; Bonnert, R. V. *J. Org. Chem.* **2003**, *68*, 5381. (c) Deng, X.; Mani, N. S. *Org. Lett.* **2006**, *8*, 3505.

(3) (a) *Handbook of Heterocyclic Chemistry*; Katritzky, A. R.; Pozharskii, A. F., Eds.; Pergamon: Oxford, **2000**. (b) Heller, S. T.; Natarajan, S. R. *Org. Lett.* **2006**, *8*, 2675. (c) Humphries, P. A.; Finefield, J. M. *Tetrahedron Lett.* **2006**, *47*, 2443. (d) Bishop, B. C. *Synthesis* **2004**, 43. (e) Ahmed, S. M.; Kobayashi, K.; Mori, A. *Org. Lett.* **2005**, *7*, 4487.

(4) For a review of cyclization reactions of dianions in organic synthesis, see: (a) Langer, P.; Freiberg, W. *Chem. Rev.* **2004**, *104*, 4125. For original papers, see: (b) Matsumura, N.; Kunigihara, A.; Yoneda, S. *Tetrahedron Lett.* **1983**, *24*, 3239. (c) Matsumura, N.; Kunigihara, A.; Yoneda, S. *Tetrahedron Lett.* **1984**, *25*, 4529. (d) Duncan, D. C.; Trumbo, T. A.; Almquist, C. D.; Lentz, T. A.; Beam, C. F. *J. Heterocycl. Chem.* **1987**, *24*, 555. (e) Beam, C. F.; Reames, D. C.; Harris, C. E.; Dasher, I. W.; Hollinger, W. M.; Shealy, N. L.; Sandifer, R. M.; Perkins, M.; Hauser, C. R. *J. Org. Chem.* **1975**, *40*, 514. (f) Persson, T.; Nielsen, J. *Org. Lett.* **2006**, *8*, 3219. (g) Dang, T. T.; Dang, T. T.; Reinke, H.; Fischer, C.; Langer, P. *Tetrahedron* **2008**, *64*, 2207.

(5) Ranatunge, R. R.; Augustyniak, M.; Bandarage, U. K.; Earl, R. A.; Ellis, J. L.; Garvey, D. S.; Janero, D. R.; Letts, L. G.; Martino, A. M.; Murty, M. G.; Richardson, S. K.; Schroeder, J. D.; Shumway, M. J.; Tam, S. W.; Trocha, A. M.; Young, D. V. *J. Med. Chem.* **2004**, *47*, 2180.

(6) For reviews of cross-coupling reactions of polyhalogenated heterocycles, see: (a) Schröter, S.; Stock, C.; Bach, T. *Tetrahedron* **2005**, *61*, 2245. (b) Schnürch, M.; Flasik, R.; Khan, A. F.; Spina, M.; Mihovilovic, M. D.; Stanetty, P. *Eur. J. Org. Chem.* **2006**, 3283.

(7) For studies from our laboratory, see: (a) Dang, T. T.; Dang, T. T.; Ahmad, R.; Reinke, H.; Langer, P. *Tetrahedron Lett.* **2008**, *49*, 1698. (b) Dang, T. T.; Villinger, A.; Langer, P. *Adv. Synth. Catal.* **2008**, *350*, 2109. (c) Hussain, M.; Nguyen, T. H.; Langer, P. *Tetrahedron Lett.* **2009**, *50*, 3929. (d) Tengho Toguem, S.-M.; Hussain, M.; Malik, I.; Villinger, A.; Langer, P. *Tetrahedron Lett.* **2009**, *50*, 4962. (e) Dang, T. T.; Dang, T. T.; Rasool, N.; Villinger, A.; Langer, P. *Adv. Synth. Catal.* **2009**, *351*, 1595.

(8) Iddon, B.; Toender, J. E.; Hosseini, M.; Begtrup, M. *Tetrahedron* **2007**, *63*, 56.

(9) For pharmacologically relevant 3,4,5-triarylpyrazoles, see: (a) Meanwell, N. A.; Rosenfeld, M. J.; Wright, J. J. K.; Brassard, C. L.; Buchanan, J. O. *J. Med. Chem.* **1992**, *35*, 389. For pharmacological relevant 3,5-diaryl-4-bromo-pyrazoles, see: (b) Bondavalli, F.; Bruno, O.; Ranise, A.; Schenone, P.; Donnoli, D. *Farmaco* **1989**, *44*, 655. (c) Bondavalli, F.; Bruno, O.; Ranise, A.; Schenone, P.; Addonizio, P. *Farmaco* **1988**, *43*, 725. Only very few 5-aryl-3,4-dibromopyrazoles have been reported so far: (d) Trofimenko, S.; Yap, G. P. A.; Jove, F. A.; Claramunt, R. M.; Garcia, M. A.; Santa Maria, M. D.; Alkorta, I.; Elguero, J. *Tetrahedron* **2007**, *63*, 8104.

(10) Grandberg, A. *J. Gen. Chem. USSR (Engl. Transl.)* **1963**, *33*, 503; *Zh. Obshch. Khim.* **1963**, *33*, 511.

(11) **General Procedure for Suzuki–Miyaura Coupling Reactions**
To a 1,4-dioxane solution (4 mL) of **2a**,**b** (152 mg, 0.5 mmol) was added $Pd(PPh_3)_4$ (3–10 mol%) at 20 °C under argon atmosphere. After stirring for 30 min, the arylboronic acid (1.0–1.2 equiv per bromine atom of the substrate), K_3PO_4 (1.5 equiv per bromine atom of the substrate), and H_2O (1.0 mL) were added. The mixture was heated for 12 h at 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).

(12) **3,4-Dibromo-5-(4-methoxyphenyl)-1-vinyl-1*H*-pyrazole (4c)**
Starting with **2b** (165 mg, 0.50 mmol), $Pd(PPh_3)_4$ (18 mg, 3 mol%), 1,4-dioxane–H_2O (4:1, 5 mL), K_3PO_4 (159 mg, 0.75 mmol), and 4-methoxyphenylboronic acid (76 mg, 0.50 mmol), **4c** was isolated as a white solid (131 mg, 73%). ^1H

NMR (300 MHz, $CDCl_3$): δ = 3.80 (s, 3 H, OCH_3), 4.77 (d, 1 H, *J* = 8.7 Hz, vinyl), 5.72 (d, 1 H, *J* = 15.2 Hz, vinyl), 6.70 (dd, 1 H, *J* = 15.2, 8.7 Hz vinylic CH), 6.95 (d, 2 H, *J* = 8.8 Hz, ArH), 7.25 (d, 2 H, *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): 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, 984 (s), 888 (m), 833 (s), 801 (m), 725 (w), 602 (m), 551 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 358 (^{81}Br, 100) $[M]^+$, 343 (13), 327 (22), 277 (39), 246 (22), 198 (23). HRMS (EI, 70 eV): *m/z* calcd for $C_{12}H_{10}N_2Br_2O$ $[M]^+$ (^{79}Br): 355.91544; found: 355.91535.

(13) Billingsley, K.; Buchwald, S. L. *J. Am. Chem. Soc.* **2007**, *129*, 3358; and references cited therein.

(14) **4-Bromo-3,5-bis(4-methoxyphenyl)-1-vinyl-1*H*-pyrazole (5a)**
Starting with **2b** (165 mg, 0.50 mmol), $Pd(PPh_3)_4$ (29 mg, 5 mol%), 1,4-dioxane–H_2O (4:1, 5 mL), K_3PO_4 (318 mg, 1.5 mmol), and 4-methoxyphenylboronic acid (152 mg, 1.0 mmol), **5a** was isolated as a white crystalline solid (115 mg, 60%). ^1H NMR (300 MHz, $CDCl_3$): δ = 3.79 (s, 3 H, OCH_3), 3.81 (s, 3 H, OCH_3), 4.75 (d, 1 H, *J* = 8.5 Hz, vinyl), 5.75 (d, 1 H, *J* = 15.4 Hz, vinyl), 6.78 (dd, 1 H, *J* = 8.8, 15.3 Hz, vinylic CH), 6.92 (d, 2 H, *J* = 8.9 Hz, ArH), 6.96 (d, 2 H, *J* = 8.8 Hz, ArH), 7.30 (d, 2 H, *J* = 8.8 Hz, ArH), 7.86 (d, 2 H, *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 (CH), 130.3, 131.7 (CH), 142.2, 149.3, 159.9, 160.4 (C). IR (KBr): 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 (^{79}Br, 3) $[M]^+$, 365 (8), 332 (7), 281 (13), 207 (100), 175 (09), 135 (04) cm^{-1}. HRMS (EI, 70 eV): *m/z* calcd for $C_{19}H_{17}N_2BrO_2$ $[M]^+$ (^{79}Br): 384.04734; found: 384.04711.

(15) CCDC-777244 contains all crystallographic details of this publication which are available free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or can be ordered from the following address: Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB21EZ; fax: +44 (1223)336033; or deposit@ccdc.cam.ac.uk.

(16) **3,4,5-Tris(3,5-dimethylphenyl)-1-vinyl-1*H*-pyrazole (6f)**
Starting with **2b** (165 mg, 0.50 mmol), $Pd(PPh_3)_4$ (58 mg, 10 mol%), 1,4-dioxane–H_2O (4:1, 5 mL), K_3PO_4 (477 mg, 2.25 mmol), and 3,5-dimethylphenylboronic acid (263 mg, 1.75 mmol), **6f** was isolated as a white solid (165 mg, 74%). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.06 (s, 6 H, 2 CH_3), 2.10 (s, 6 H, 2 CH_3), 2.15 (s, 6 H, 2 CH_3), 4.69 (d, 1 H, *J* = 8.7 Hz, vinyl), 5.78 (d, 1 H, *J* = 15.3 Hz, vinyl), 6.61–6.90 (m, 8 H), 7.09 (br s, 2 H, ArH). ^{13}C NMR (75.5 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): 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 (100) $[M]^+$, 391 (26), 375 (2), 259 (4), 203 (3), 180 (2), 132 (4). HRMS (EI, 70 eV): *m/z* calcd for $C_{29}H_{30}N_2$ $[M]^+$: 406.24090; found: 406.24057.