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Catalytic System for Inhibition of Amination-Type Reaction and Palladium-Catalysed Direct Arylation using Non-Protected Pyrazole Derivatives

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Abstract: The palladium-catalysed direct arylation at C-4 of non-protected 5-aminopyrazoles was found to proceed in high yields using a variety of aryl bromides. The choice of potassium acetate as the base was found to be crucial to inhibit the amination reaction and to promote the direct arylation.

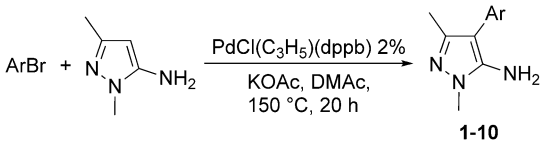
Keywords: atom economy; catalysis; C–H activation; heteroarenes; palladium

Mixed bi(hetero)aryl derivatives display a set of bioactive or physical properties and their preparation constitutes an active field of research in organic chemistry.[1] In recent years, the palladium-catalysed direct arylation of heteroaromatics has emerged as a very powerful method for the preparation of arylated heteroaromatics.[2–7] However, there are still limitations for these reactions in terms of functional group tolerance of the heteroaromatic compound. While the presence of acetyl, formyl, nitrile, and methyl alcohol as the functional groups on the thiophenes has been described,[8] on the other hand, the use of free NH_2 substituents has attracted much less attention. To the best of our knowledge, only purines bearing a free NH_2 on the six-membered ring have been employed.[9,10] In a few cases, protected amines have been used.[11–15]

However, the direct use of heteroaromatics bearing unprotected functions, such as NH_2 would be more useful in organic synthesis since it would allow one to avoid the *protection/deprotection sequence*, and would provide a more environmentally and economically attractive access to such arylated heteroaromatics. Therefore, the discovery of effective conditions, for the direct coupling of such heteroaromatics with aryl halides, would be a considerable advantage for industrial applications and for sustainable development.

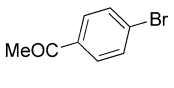
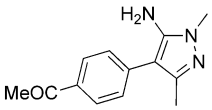
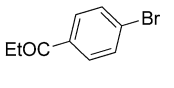
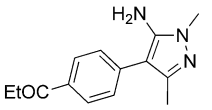
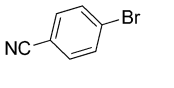
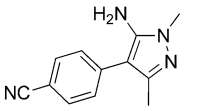
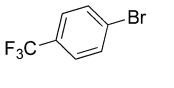
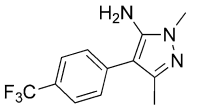
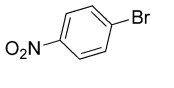
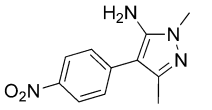
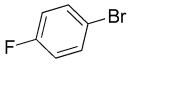
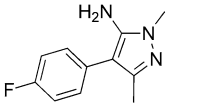
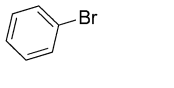
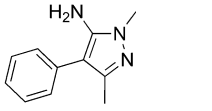
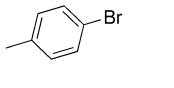
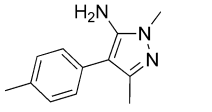
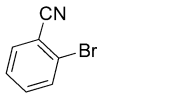
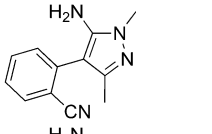
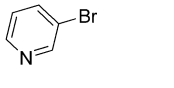
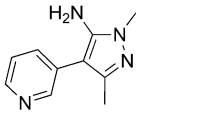
We have recently reported results on the direct arylation of some free NH_2 substituted thiophenes.[16] In this update, we wish to report on the reaction of pyrazoles derivatives bearing unprotected amino functions with a set of electronically and sterically diverse aryl bromides.

The direct arylation of heteroaromatics bearing a free NH_2 is not limited to the use of thiophenes. Pyrazoles were also found to be suitable reactants (Scheme 1, Scheme 2, and Table 1). We observed that 1,3-dimethylpyrazol-5-amine in the presence of 2 mol% $PdCl(C_3H_5)$(dppb), KOAc as the base and 4-bromoacetophenone led to the C.4 arylated pyrazole **1** in a high yield of 85% (Table 1, entry 1). It should be noted that, under these reaction conditions, no arylation at the NH_2 group was observed. Quite similar results were obtained in the presence of 4-bromopropiophenone, 4-bromobenzonitrile or 4-(trifluoromethyl)bromobenzene, and products **2–4** were obtained in 64–83% yields (Table 1, entries 2–4). A lower yield of 48% in **5** was obtained with 4-bromonitrobenzene due to the formation of side-products (Table 1, entry 5). 4-Fluorobromobenzene, bromobenzene, 4-bromotoluene or 2- bromobenzonitrile also led to the direct arylation products **6–9** in moderate yields due to partial conversions of these aryl bromides (Table 1,



Scheme 1.

Table 1. Direct arylations of 1,3-dimethylpyrazol-5-amine (Scheme 1).[a]

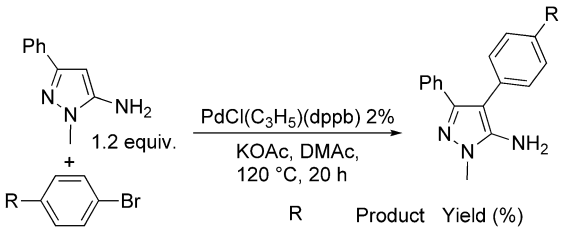
Entry	Aryl bromide	Product		Yield [%]
1			**1**	85
2			**2**	64
3			**3**	83
4			**4**	70
5			**5**	48
6			**6**	40
7			**7**	20
8			**8**	43
9			**9**	21
10			**10**	52

[a] *Reaction conditions:* $PdCl(C_3H_5)(dppb)$ (0.02 equiv.), aryl bromide (1 equiv.), 1,3-dimethylpyrazol-5-amine (2 equiv.), KOAc (2 equiv.), DMAc, 20 h, 150 °C.

entries 6–9). A yield of 52% in **10** was obtained in the presence of 3-bromopyridine (Table 1, entry 10).

The reactivity of a pyrazole substituted at C-3 by a phenyl and at C-5 by a free NH_2 was also examined (Scheme 2). This substrate was found to be slightly less reactive than 1,3-dimethylpyrazol-5-amine. However, the desired C-4 arylated products **11**–**13** were obtained in 42–62% yield.

In summary, we have demonstrated that when appropriate reaction conditions are employed, the palladium-catalysed direct arylations at C-4 of some free NH_2 substituted pyrazole derivatives with aryl bromides proceed nicely. The choice of KOAc as the



R	Product	Yield (%)
CF_3	**11**	62
CN	**12**	60
NO_2	**13**	42

Scheme 2.

base inhibits the amination reaction and promotes the direct arylation. This result is consistent with a concerted metallation-deprotonation mechanism.[17] A wide variety of substituents such as acetyl, propionyl, nitrile, nitro, trifluoromethyl, or fluoro on the aryl bromide is tolerated. To the best of our knowledge, this is the first method for direct arylation of free NH_2 subsituted pyrazoles. This procedure is attractive as it allows one to prepare arylated pyrazoles bearing free NH_2 substituents without a protection/deprotection sequence and therefore should provide a "greener" and more economic access to such compounds.

Experimental Section

General Remarks

All reactions were performed in Schlenck tubes under argon. DMAc analytical grade was not distilled before use. Potassium acetate 99+ was used. Commercial aryl bromides and heteroaromatic derivatives were used without purification. ^1H (300 MHz), ^{13}C NMR (75 MHz) spectra were recorded in $CDCl_3$ solutions. Chemical shifts are reported in ppm relative to $CDCl_3$ (^1H: 7.26 and ^{13}C: 77.0). Flash chromatography was performed on silica gel (230–400 mesh).

General Procedure for the Synthesis of Products 1–13

As a typical experiment, the reaction of the aryl bromide (1 mmol), the pyrazole derivative (2 mmol) and KOAc (0.196 g, 2 mmol) at 120–150 °C during 20 h in DMAc (3 mL) in the presence of $PdCl(C_3H_5)(dppb)$ (12.2 mg, 0.02 mmol) under argon afforded the coupling product after extraction with dichloromethane, evaporation and filtration on silica gel (pentane/ether).

1-[4-(5-Amino-1,3-dimethylpyrazol-4-yl)phenyl]ethanone (1): 4-Bromoacetophenone (0.199 g, 1 mmol), 1,3-dimethylpyrazol-5-amine (0.222 g, 2 mmol) and KOAc (0.196 g, 2 mmol) at 150 °C during 20 h in DMAc (3 mL) in the presence of $PdCl(C_3H_5)(dppb)$ (12.2 mg, 0.02 mmol) under argon afforded **1**; yield: 0.195 g (85%).

1-[4-(5-Amino-1,3-dimethylpyrazol-4-yl)phenyl]propan-1-one (2): 4-Bromopropiophenone (0.213 g, 1 mmol), 1,3-dimethylpyrazol-5-amine (0.222 g, 2 mmol) and KOAc (0.196 g, 2 mmol) at 150 °C during 20 h in DMAc (3 mL) in

the presence of $PdCl(C_3H_5)$(dppb) (12.2 mg, 0.02 mmol) under argon afforded **2**; yield: 0.155 g (64%).

4-(5-Amino-1,3-dimethylpyrazol-4-yl)benzonitrile (3): 4-Bromobenzonitrile (0.182 g, 1 mmol), 1,3-dimethylpyrazol-5-amine (0.222 g, 2 mmol) and KOAc (0.196 g, 2 mmol) at 150 °C during 20 h in DMAc (3 mL) in the presence of $PdCl(C_3H_5)$(dppb) (12.2 mg, 0.02 mmol) under argon afforded **3**; yield: 0.176 g (83%).

1,3-Dimethyl-4-[4-(trifluoromethyl)phenyl]pyrazol-5-ylamine (4): 4-(Trifluoromethyl)bromobenzene (0.225 g, 1 mmol), 1,3-dimethylpyrazol-5-amine (0.222 g, 2 mmol) and KOAc (0.196 g, 2 mmol) at 150 °C during 20 h in DMAc (3 mL) in the presence of $PdCl(C_3H_5)$(dppb) (12.2 mg, 0.02 mmol) under argon afforded **4**; yield: 0.178 g (70%).

1,3-Dimethyl-4-(4-nitrophenyl)pyrazol-4-ylamine (5): 4-Bromonitrobenzene (0.202 g, 1 mmol), 1,3-dimethylpyrazol-5-amine (0.222 g, 2 mmol) and KOAc (0.196 g, 2 mmol) at 150 °C during 20 h in DMAc (3 mL) in the presence of $PdCl(C_3H_5)$(dppb) (12.2 mg, 0.02 mmol) under argon afforded **5**; yield: 0.111 g (48%).

4-(4-Fluorophenyl)-1,3-dimethylpyrazol-5-ylamine (6): 4-Bromofluorobenzene (0.175 g, 1 mmol), 1,3-dimethylpyrazol-5-amine (0.222 g, 2 mmol) and KOAc (0.196 g, 2 mmol) at 150 °C during 20 h in DMAc (3 mL) in the presence of $PdCl(C_3H_5)$(dppb) (12.2 mg, 0.02 mmol) under argon afforded **6**; yield: 0.083 g (40%).

1,3-Dimethyl-4-phenylpyrazol-5-ylamine (7):[18] Bromobenzene (0.157 g, 1 mmol), 1,3-dimethylpyrazol-5-amine (0.222 g, 2 mmol) and KOAc (0.196 g, 2 mmol) at 150 °C during 20 h in DMAc (3 mL) in the presence of $PdCl(C_3H_5)$(dppb) (12.2 mg, 0.02 mmol) under argon afforded **7**; yield: (0.037 g (20%).

1,3-Dimethyl-4-*p*-tolylpyrazol-5-ylamine (8): 4-Bromotoluene (0.171 g, 1 mmol), 1,3-dimethylpyrazol-5-amine (0.222 g, 2 mmol) and KOAc (0.196 g, 2 mmol) at 150 °C during 20 h in DMAc (3 mL) in the presence of $PdCl(C_3H_5)$(dppb) (12.2 mg, 0.02 mmol) under argon afforded **8**; yield: 0.086 g (43%).

2-(5-Amino-1,3-dimethylpyrazol-4-yl)benzonitrile (9): 2-Bromobenzonitrile (0.182 g, 1 mmol), 1,3-dimethylpyrazol-5-amine (0.222 g, 2 mmol) and KOAc (0.196 g, 2 mmol) at 150 °C during 20 h in DMAc (3 mL) in the presence of $PdCl(C_3H_5)$(dppb) (12.2 mg, 0.02 mmol) under argon afforded **9** ; yield: 0.045 g (21%).

1,3-Dimethyl-4-(pyridin-3-yl)pyrazol-5-ylamine (10): 3-Bromopyridine (0.158 g, 1 mmol), 1,3-dimethylpyrazol-5-amine (0.222 g, 2 mmol) and KOAc (0.196 g, 2 mmol) at 150 °C during 20 h in DMAc (3 mL) in the presence of $PdCl(C_3H_5)$(dppb) (12.2 mg, 0.02 mmol) under argon afforded **10**; yield: 0.098 g (52%).

2-Methyl-5-phenyl-4-(4-trifluoromethylphenyl)pyrazol-3-ylamine (11): 4-(Trifluoromethyl)bromobenzene (0.225 g, 1 mmol), 1-methyl-3-phenylpyrazol-5-amine (0.207 g, 1.2 mmol) and KOAc (0.196 g, 2 mmol) at 120 °C during 20 h in DMAc (3 mL) in the presence of $PdCl(C_3H_5)$(dppb) (12.2 mg, 0.02 mmol) under argon afforded **11**; yield: (0.197 g (62%).

4-(5-Amino-1-methyl-3-phenylpyrazol-4-yl)benzonitrile (12): 4-Bromobenzonitrile (0.182 g, 1 mmol), 1-methyl-3-phenylpyrazol-5-amine (0.207 g, 1.2 mmol) and KOAc (0.196 g, 2 mmol) at 120 °C during 20 h in DMAc (3 mL) in the presence of $PdCl(C_3H_5)$(dppb) (12.2 mg, 0.02 mmol) under argon afforded **12**; yield: 0.165 g (60%).

2-Methyl-4-(4-nitrophenyl)-5-phenylpyrazol-3-ylamine (13): 4-Bromonitrobenzene (0.202 g, 1 mmol), 1-methyl-3-phenylpyrazol-5-amine (0.207 g, 1.2 mmol) and KOAc (0.196 g, 2 mmol) at 120 °C during 20 h in DMAc (3 mL) in the presence of $PdCl(C_3H_5)$(dppb) (12.2 mg, 0.02 mmol) under argon afforded **13**; yield: 0.123 g (42%).

Acknowledgements

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References

[1] a) J. J. Li, G. W. Gribble, *Palladium in Heterocyclic Chemistry*, Pergamon, Amsterdam, **2000**; b) E. Negishi, (Ed.), *Handbook of Organopalladium Chemistry for Organic Synthesis*, Wiley-Interscience, New York, **2002**; Part III, p 213; c) J. Hassan, M. Sevignon, C. Gozzi, E. Schulz, M. Lemaire, *Chem. Rev.* **2002**, *102*, 1359.

[2] a) D. Alberico, M. E. Scott, M. Lautens, *Chem. Rev.* **2007**, *107*, 174; b) T. Satoh, M. Miura, *Chem. Lett.* **2007**, *36*, 200; c) I. V. Seregin, V. Gevorgyan, *Chem. Soc. Rev.* **2007**, *36*, 1173; d) B.-J. Li, S.-D. Yang, Z.-J. Shi, *Synlett* **2008**, 949; e) G. P. McGlacken, L. M. Batman, *Chem. Soc. Rev.* **2009**, *38*, 2447; f) F. Bellina, R. Rossi, *Tetrahedron* **2009**, *65*, 10269; g) L. Ackermann, R. Vincente, A. R. Kapdi, *Angew. Chem.* **2009**, *121*, 9976; *Angew. Chem. Int. Ed.* **2009**, *48*, 9792; h) J. Roger, A. L. Gottumukkala, H. Doucet, *ChemCatChem* **2010**, *2*, 20; i) C. Fischmeister, H. Doucet, *Green Chem.* **2011**, *13*, 741.

[3] A. Ohta, Y. Akita, T. Ohkuwa, M. Chiba, R. Fukunaga, A. Miyafuji, T. Nakata, N. Tani, Y. Aoyagi, *Heterocycles* **1990**, *31*, 1951.

[4] For selected recent examples of palladium-catalysed direct arylations from our laboratory: a) A. L. Gottumukkala, H. Doucet, *Adv. Synth. Catal.* **2008**, *350*, 2183; b) J. J. Dong, J. Roger, F. Požgan, H. Doucet, *Green Chem.* **2009**, *11*, 1832; c) R. V. Smaliy, M. Beaupérin, H. Cattey, P. Meunier, J.-C. Hierso, J. Roger, H. Doucet, Y. Coppel, *Organometallics* **2009**, *28*, 3152; d) Y. Fall, H. Doucet, M. Santelli, *ChemSusChem* **2009**, *2*, 153; e) J. Roger, H. Doucet, *Adv. Synth. Catal.* **2009**, *351*, 1977; f) Y. Fall, C. Reynaud, H. Doucet, M. Santelli, *Eur. J. Org. Chem.* **2009**, 4041; g) J. J. Dong, J. Roger, C. Verrier, T. Martin, R. Le Goff, C. Hoarau, H. Doucet, *Green Chem.* **2010**, *12*, 2053.

[5] For recent examples of direct arylations of thiophenes: a) E. David, S. Pellet-Rostaing, M. Lemaire, *Tetrahedron* **2007**, *63*, 8999; b) P. Amaladass, J. A. Clement, A. K. Mohanakrishnan, *Tetrahedron* **2007**, *63*, 10363; c) H. A. Chiong, O. Daugulis, *Org. Lett.* **2007**, *9*, 1449; d) M. Nakano, H. Tsurugi, T. Satoh, M. Miura, *Org. Lett.* **2008**, *10*, 1851; e) M. Nakano, H. Tsurugi, T.

Satoh, M. Miura, *Org. Lett.* **2008**, *10*, 1851; f) F. Derridj, J. Roger, F. Geneste, S. Djebbar, H. Doucet, *J. Organomet. Chem.* **2009**, *694*, 455; g) F. Shibahara, E. Yamaguchi, T. Murai, *Chem. Commun.* **2010**, *46*, 2471; h) S. Yanagisawa, K. Ueda, H. Sekizawa, K. Itami, *J. Am. Chem. Soc.* **2009**, *131*, 14622; i) K. Ueda, S. Yanagisawa, J. Yamaguchi, K. Itami, *Angew. Chem.* **2010**, *122*, 9130; *Angew. Chem. Int. Ed.* **2010**, *49*, 8946.

[6] For recent examples of direct arylations of pyrazoles: a) E. J. Brnardic, R. M. Garbaccio, M. E. Fraley, E. S. Tasber, J. T. Steen, K. L. Arrington, V. Y. Dudkin, G. D. Hartman, S. M. Stirdivant, B. A. Drakas, K. Rickert, E. S. Walsh, K. Hamilton, C. A. Buser, J. Hardwick, W. Tao, S. C. Beck, X. Mao, R. B. Lobell, L. Sepp-Lorenzino, Y. Yan, M. Ikuta, S. K. Munshi, L. C. Kuo, C. Kreatsoulas, *Bioorg. Med. Chem. Lett.* **2007**, *17*, 5989; b) R. Goikhman, T. L. Jacques, D. Sames, *J. Am. Chem. Soc.* **2009**, *131*, 3042; c) C. Mateos, J. Mendiola, M. Carpintero, J. M. Minguez, *Org. Lett.* **2010**, *12*, 4924; d) Y. L. Choi, H. Lee, B. T. Kim, K. Choi, J.-N. Heo, *Adv. Synth. Catal.* **2010**, *352*, 2041; e) F. Shibahara, E. Yamaguchi, T. Murai, *J. Org. Chem.* **2011**, *76*, 2680.

[7] For examples of palladium-catalysed direct 4-arylations of pyrazoles: a) S. Kumar, H. Ila, H. Junjappa *J. Org. Chem.* **2009**, *74*, 7046; b) Y. Fall, H. Doucet, M. Santelli *Synthesis* **2010**, 127.

[8] For examples of palladium-catalysed direct arylations using thiophenes bearing formyl, acetyl, nitrile, silyl, halo or methyl alcohol substituents: a) S. Pivsa-Art, T. Satoh, Y. Kawamura, M. Miura, M. Nomura, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 467; b) L. Lavenot, C. Gozzi, K. Ilg, I. Orlova, V. Penalva, M. Lemaire, *J. Organomet. Chem.* **1998**, *567*, 49; c) T. Okazawa, T. Satoh, M. Miura, M. Nomura, *J. Am. Chem. Soc.* **2002**, *124*, 5286; d) J. Hassan, C. Gozzi, E. Schulz, M. Lemaire, *J. Organomet. Chem.* **2003**, *687*, 280; e) K. Masui, H. Ikegami, A. Mori, *J. Am. Chem. Soc.* **2004**, *126*, 5074; f) K. Kobayashi, A. Sugie, M. Takahashi, K. Masui, A. Mori, *Org. Lett.* **2005**, *7*, 5083; g) K. Kobayashi, M. S. Mohamed Ahmed, A. Mori, *Tetrahedron* **2006**, *62*, 9548; h) J. Roger, F. Požgan, H. Doucet, *Green Chem.* **2009**, *11*, 425; i) B. Liégault, D. Lapointe, L. Caron, A. Vlassova, K. Fagnou, *J. Org. Chem.* **2009**, *74*, 1826; j) J. J. Dong, J. Roger, H. Doucet, *Tetrahedron Lett.* **2009**, *50*, 2778; k) J. Roger, F. Požgan, H. Doucet, *Adv. Synth. Catal.* **2010**, *352*, 696; l) B. Liégault, I. Petrov, S. I. Gorlesky, K. Fagnou, *J. Org. Chem.* **2010**, *75*, 1047; m) O. Rene, K. Fagnou, *Org. Lett.* **2010**, *12*, 2116; n) K. Beydoun, H. Doucet, *ChemSusChem* **2011**, *4*, 526; o) L. Chen, J. Roger, C. Bruneau, P. H. Dixneuf, H. Doucet, *Chem. Commun.* **2011**, *47*, 1872; p) D. J. Schipper, K. Fagnou *Chem. Mater.* **2011**, *23*, 1594.

[9] For examples of palladium-catalysed direct arylations using free-(NH_2) adenines: S. Sahnoun, S. Messaoudi, J.-D. Brion, M. Alami, *Org. Biomol. Chem.* **2009**, *7*, 4271.

[10] For examples of palladium-catalysed direct arylations using purines: a) I. Cerna, R. Pohl, M. Hocek, *Chem. Commun.* **2007**, 4729; b) T. E. Storr, A. G. Firth, K. Wilson, K. Darley, C. G. Baumann, I. J. S. Fairlamb, *Tetrahedron* **2008**, *64*, 6125; c) I. Cerna, R. Pohl, B. Klepetarova M. Hocek, *J. Org. Chem.* **2008**, *73*, 9048; d) T. E. Storr, C. G. Baumann, R. J. Thatcher, S. De Ornellas, A. C. Whitwood, I. J. S. Fairlamb, *J. Org. Chem.* **2009**, *74*, 5810; e) I. Cerna, R. Pohl, B. Klepetarova, M. Hocek, *J. Org. Chem.* **2010**, *75*, 2302; f) T. E. Storr, J. A. Strohmeier, C. G. Baumann, I. J. S. Fairlamb, *Chem. Commun.* **2010**, *46*, 6470.

[11] For intramolecular cyclisations of aniline derivatives, see: L. Ackermann, A. Althammer, P. Mayer, *Synthesis* **2009**, 3493.

[12] For examples of palladium-catalysed direct arylations using protected 2-aminothiazoles, see: a) J. Priego, S. Gutierrez, R. Ferritto, H. B. Broughton, *Synlett* **2007**, 2957; b) H. A. Chiong, O. Daugulis, *Org. Lett.* **2007**, *9*, 1449.

[13] For an example of palladium-catalysed intramolecular direct arylations using a protected 2-aminofuran, see: A. Padwa, M. A. Brodney, S. M. Lynch, *J. Org. Chem.* **2001**, *66*, 1716.

[14] For examples of palladium-catalysed direct arylations using protected 2- or 3-aminothiophenes: a) E. M. Beccalli, G. Broggini, M. Martinelli, S. Sottocornola, *Synthesis* **2008**, 136; b) J. Roger, H. Doucet, *Eur. J. Org. Chem.* **2010**, 4412.

[15] For an example of palladium-catalysed intramolecular direct arylation using an aminothiophene derivative: I. C. F. R. Ferreira, M.-J. R. P. Queiroz, G. Kirsch, *Tetrahedron* **2003**, *59*, 3737.

[16] F. Derridj, J. Roger, S. Djebbar, H. Doucet, *Org. Lett.* **2010**, *12*, 4320.

[17] a) D. L. Davies, S. M. A. Donald, S. A. Macgregor, *J. Am. Chem. Soc.* **2005**, *127*, 13754; b) D. Lapointe, K. Fagnou, *Chem. Lett.* **2010**, *39*, 1118.

[18] T. Ryckmans, H.-G. Viehe, *Tetrahedron* **1997**, *53.* 1729.

