Scope and Limitations of the Base-Free Copper(I) Oxide Catalyzed *N*-Heteroarylation of 1*H*-(Benz)imidazoles with *B*-Heteroarylboronic Acids or 2-Heteroaryl-4,4,5,5-tetramethyl-1,3,2-dioxaborolanes

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The known, very efficient base-free copper(I) oxide catalyzed *N*-arylation reaction performed in MeOH at room temperature for the synthesis of *N*-substituted azoles and amines was extended to the heterocyclic series, i.e., we report herein the base-free copper(I) oxide catalyzed *N*-heteroarylation of 1*H*-(benz)imidazole, by means of electron-rich or electron-deficient *B*-heteroarylboronic acids or 2-heteroaryl-4,4,5,5-tetramethyl-1,3,2-dioxaborolanes (*Schemes 1* and *2*). Under these conditions, *N*-heteroarylated 1*H*-(benz)imidazoles were obtained in good to excellent yields (*Tables 1* and *2*). This is the first time that 2-heteroaryl-4,4,5,5-tetramethyl-1,3,2-dioxaborolanes were used in this type of reaction.

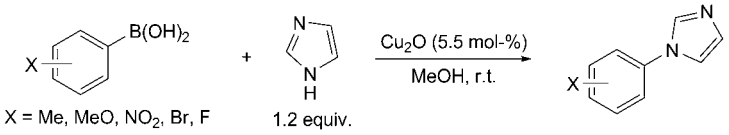
Introduction. – *N*-Arylated azoles and amines are found in many biologically active compounds [1]. The synthesis of these compounds includes the copper-mediated *Ullmann* coupling [2] and the palladium-catalyzed *Buchwald–Hartwig* reactions [3]. These methodologies are very effective, but the use of *B*-arylboronic acids was shown to be a significant improvement.

The development of mild and efficient methods for the synthesis of 1-aryl-1*H*-imidazoles from *B*-arylboronic acids by using copper species as the catalysts has gained considerable attention [4–11]. Thus, in 1998, the *Chan* and *Lam*'*s* group have described the synthesis of *N*-arylated azoles from *B*-arylboronic acids in the presence of $Cu(OAc)_2$ as the catalyst and pyridine as the base at room temperature [4], and in 1999 *Combs* and co-workers have reported the first examples of this reaction performed on a polymer support [5]. $Cu(OAc)_2$ was also used by *Boatman et al.* [6] together with Et_3N as the base, CH_2Cl_2 as the solvent, and molecular sieves for the synthesis of *N*-(hetero)arylated 3*H*-imidazo[4,5-*b*]pyridin-5-ol derivatives useful in the treatment of GPR81 receptor disorders. The copper complex $[Cu(OH)\cdot(tmeda)]_2Cl_2$ (tmeda = N^1,N^1,N^2,N^2-tetramethylethane-1,2-diamine) has been used by *Collman* and co-workers in the same reaction, with H_2O or CH_2Cl_2 as solvents [7]. The use of a Cu^IX has also been reported by *Lan* and co-workers, in MeOH or aqueous solutions [8]. *Tromp* and co-workers have recently studied the mechanism of the copper(II) catalyzed *N*-arylation of 1*H*-imidazole [9]. All these reactions were performed under air or O_2 atmosphere, as it seems that this reaction takes place following a redox mechanism.

Copper heterogeneous catalysts feature low toxicity and low cost, allow the production of a large quantity of products and can be recycled, hence the interest of

their utilization. In 2008, *Sreedhar* and co-workers have developed a mild and efficient method for the *N*-arylation of 1*H*-imidazole or 1*H*-benzimidazole with *B*-arylboronic acids catalyzed by the heterogeneous copper(I) species Cu_2O, under base-free conditions at room temperature in MeOH (*Scheme 1*) affording the expected *N*-substituted arylazoles in good to excellent yields [10]. They were able to recover Cu_2O quantitatively by simple centrifugation and to reuse it with no loss of activity for four cycles. Here again, no particular precaution had to be taken to avoid contact with air and H_2O. It appeared that no coupled product was formed in the absence of air.

Scheme 1. N-*Arylation of 1*H-*(Benz)imidazoles in the Presence of Cu_2O as a Heterogeneous Catalyst*



Kantam and co-workers have reported the use of another heterogeneous copper catalyst, CuFAP (copper(II) fluoroapatite), for the *N*-arylation of 1*H*-imidazole, 1*H*-benzimidazole, and amines with *B*-arylboronic acids under similar conditions (no base, at room temperature, in MeOH) [11a]. More recently, the same group extended the use of CuFAP to the *N*-arylation of azoles with *B*-aryl-, *B*-vinyl-, and *B*-heteroarylboronic acids (*B*-thienyl- and *B*-furanylboronic acids) [11b]. With this system, they were always able to obtain the expected products in good to excellent yields.

As far as we know, the use of a heterogeneous copper species as the catalyst and *B*-heteroarylboronic acids as the starting materials in this reaction has only been reported by *Kantam*'s [11b] and *Boatman*'s [6] groups, and the utilization of the commercially available Cu_2O in the *N*-heteroarylation of azoles involving *B*-heteroarylboronic acids has not been studied yet. Moreover, the use of 2-heteroaryl-4,4,5,5-tetramethyl-1,3,2-dioxaborolanes as the starting materials instead of the corresponding boronic acids has never been reported. Herein, we present the synthesis of various *N*-heteroaryl-1*H*-(benz)imidazoles from electron-rich and electron-deficient *B*-heteroarylboronic acids or 2-heteroaryl-4,4,5,5-tetramethyl-1,3,2-dioxaborolanes in the presence of Cu_2O, as an extension of the scope of *Sreedhar*'s conditions.

Results and Discussion. – Our research group has got a solid experience in the synthesis and functionalization of thiophene and benzo[*b*]thiophene derivatives by Pd and/or Cu-catalyzed C–N *Buchwald–Hartwig* [12] and C–C *Suzuki* [13] and *Sonogashira* [14] couplings. Therefore, we first studied the synthesis of *1*-thienyl-1*H*-(benz)imidazoles or *1*-benzothienyl-1*H*-(benz)imidazoles from the electron-rich *B*-3-thienylboronic acid and *B*-benzo[*b*]thien-3-ylboronic acids as starting materials (*Table 1*, *Entries 1–4*). The corresponding *1*-(benzo)thien-3-yl-1*H*-(benz)imidazoles

1–**4** were successfully synthesized in high to excellent yields (77–92%)[1]). Similar results were obtained when the *B*-furan-3-ylboronic acid and *B*-dibenzofuran-4-ylboronic acid were used (*Entries 9–12*) affording compounds **9**–**12** in high to excellent yields[2]).

From *B*-dibenzothien-4-ylboronic acid and 1*H*-benzimidazole (*Table 1*, *Entry 5*), compound **5** was obtained in a quantitative yield at room temperature overnight, while the reaction with 1*H*-imidazole (*Entry 6*) gave compound **6** in 80% yield after 5 h. Thianthren-1-ylboronic acid was also used as starting material in this reaction (*Entries 7* and *8*) affording compounds **7** and **8** in quantitative and 83% yields, respectively.

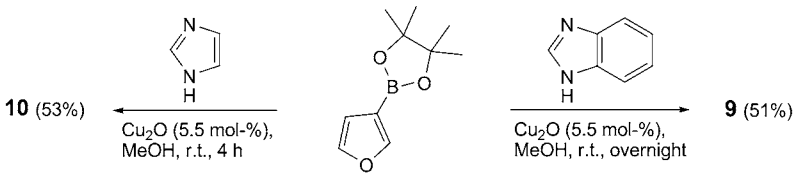
It is noteworthy that, in all cases, the best yields were obtained from 1*H*-benzimidazole allowing the mixture to be stirred overnight. With 1*H*-imidazole, the reaction times were much shorter (consumption of the boronic acid was completed within 4–5 h) but the yields were also slightly lower, and stirring the mixture for a longer time did not afford better results.

Compounds **1** and **2** were already obtained from 3-iodo-or 3-bromobenzo[*b*]thiophene and 1*H*-benzimidazole or 1*H*-imidazole, with copper as the catalyst (CuI or Cu_2O, resp.) and Cs_2CO_3 in the presence of phenantroline [15] or 4,7-dimethoxy-1,10-phenanthroline [16] as the ligands.

At this time, we thought that one possible explanation for the disappointing results obtained with the 2-substituted *B*-heteroarylboronic acids might be that these compounds are known to be of limited stability. As the corresponding 4,4,5,5-tetramethyl-1,3,2-dioxaborolanes are much more stable, we therefore investigated their use as the starting materials in this *N*-arylation reaction.

The reactions of 2-(furan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane were first carried out (*Scheme 2*) and afforded compounds **9** and **10** in good yields (51 and 53%, resp.) [11b]. Attempts to increase the yields (by heating and/or increasing the amount of catalyst) remained unsuccessful. Although these yields were lower than those

Scheme 2. N-*Heteroarylation of 1*H-*Imidazole and 1*H-*Benzimidazole from 2-(Furan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane*



[1]) With Cu^{II}FAP as the catalyst, *Kantam* and co-workers have reported that the use of *B*-2-thienylboronic acid afforded lower yields of the corresponding product compared to the use of *B*-thienylboronic acid [11b]. In our case, *B*-benzo[*b*]thien-2-ylboronic acid and *B*-2-thienylboronic acid yielded only traces of the expected *N*-heteroarylated 1*H*-(benz)imidazoles, and the starting materials were recovered at the end of the reactions, together with other nonidentified by-products.

[2]) Here again, we observed that reactions with the corresponding 2-substituted *B*-heteroarylboronic acids, *i.e.*, *B*-benzo[*b*]furan-2-ylboronic acid and *B*-furan-2-ylboronic acid, did not afford the expected compounds.

Table 1. N-*Heteroarylation of* 1*H*-*(Benz)imidazoles with* B-*Heteroarylboronic Acids*[a])

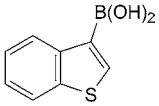
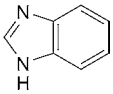
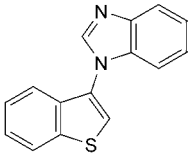
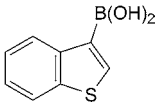
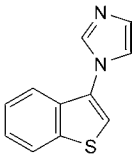
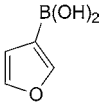
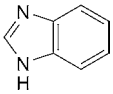
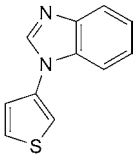
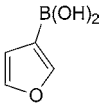
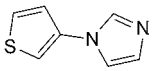
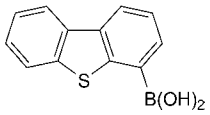
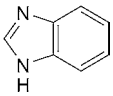
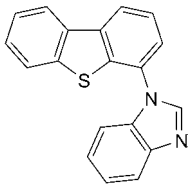
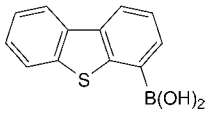
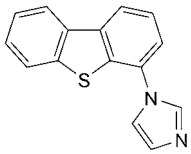
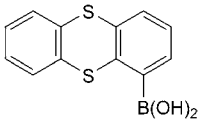
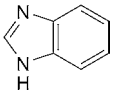
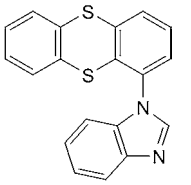
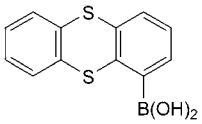
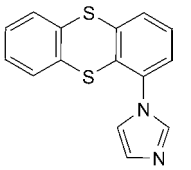
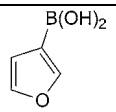
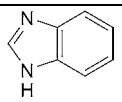
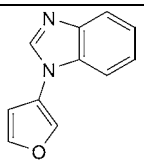
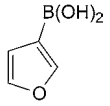
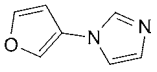
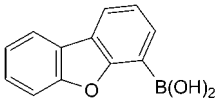
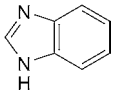
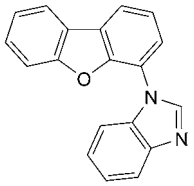
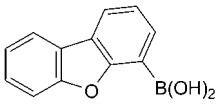
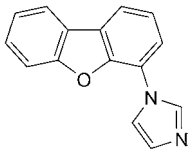
Entry	Boronic acid	1*H*-(Benz)imidazole	Reaction time	Product	Yield [%]
1			overnight		**1** 92 [15]
2			5 h		**2** 79 [16]
3			overnight		**3** 91 [11b]
4			4 h		**4** 77 [11b]
5			overnight		**5** 100
6			5 h		**6** 80
7			overnight		**7** 100
8			5 h		**8** 83

Table 1 (cont.)

Entry	Boronic acid	1*H*-(Benz)imidazole	Reaction time	Product	Yield [%]
9			overnight		**9** 79 [11b]
10			4 h		**10** 71 [11b]
11			overnight		**11** 98
12			5 h		**12** 76

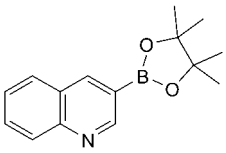
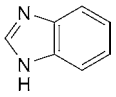
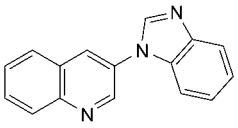
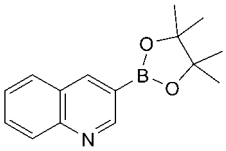
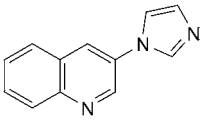
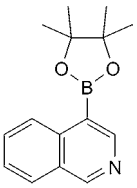
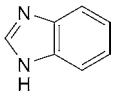
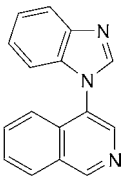
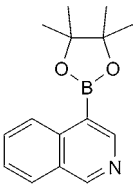
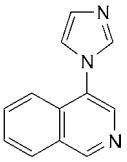
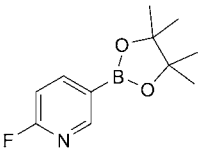
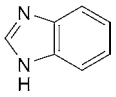
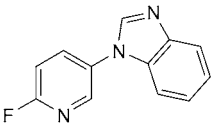
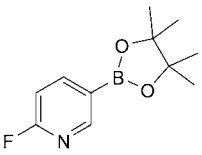
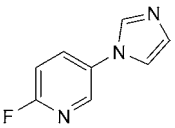
[a]) Conditions: boronic acid (1.0 equiv.), 1*H*-(benz)imidazole (1.2 equiv.), Cu_2O (5.5 mol-%), MeOH, r.t.

obtained from *B*-furan-3-ylboronic acid (79 and 71%, resp.), these results demonstrate that the use of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane derivatives is also possible under these conditions.

To extend the scope of their use, we studied the reactivity of some electron-deficient 2-heteroaryl-4,4,5,5-tetramethyl-1,3,2-dioxaborolanes (*Table 2*). The 2-(quinolin-3-yl)-substituted 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (*Table 2*, *Entries 1* and *2*) and 2-(isoquinolin-4-yl)-substituted 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (*Entries 3* and *4*) gave the corresponding *N*-heteroarylated 1*H*-(benz)imidazoles **13**–**16** in high yields (78–84%), almost in the same range than those obtained from the electron-rich derivatives. From the more electron-deficient 2-fluoro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (*Entries 5* and *6*), products **17** and **18** were synthesized only in moderate to good yields. In this particular case, it is worth to note that the 4-fluoropyridin-3-yl moiety may not be a very good candidate for this type of reaction as it is electron-deficient and that the presence of the F-atom at the pyridine ring may deactivate it even more.

Having these results in hand, we used the 2-(benzo)thien-2-yl- and 2-(benzo)furan-2-yl-4,4,5,5-tetramethyl-1,3,2-dioxaborolanes, however, once again only traces of the expected *N*-heteroarylated 1*H*-(benz)imidazoles were observed. This result definitely

Table 2. *Reaction of 1*H-*(Benz)imidazole with Various Electron-Deficient 2-Heteroaryl-4,4,5,5-tetramethyl-1,3,2-dioxaborolanes*[a])

Entry	Dioxaborolane	(Benz)imidazole	Time	Product	Yield [%]
1			overnight		**13** 81
2			6 h		**14** 78
3			overnight		**15** 78
4			6 h		**16** 84
5			overnight		**17** 54
6			6 h		**18** 43

[a]) Conditions: 2-heteroaryl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1 equiv.), 1*H*-(benz)imidazole (1.2 equiv.), Cu_2O (5.5 mol-%), MeOH, r.t.

constitutes a limitation to the use of Cu_2O as the catalyst in this *N*-(hetero)arylation methodology.

Conclusions. – We extended the scope of the base-free Cu_2O-catalyzed *N*-arylation of 1*H*-(benz)imidazoles to their *N*-heteroarylation by using *B*-heteroarylboronic acids or 2-heteroaryl-4,4,5,5-tetramethyl-1,3,2-dioxaborolanes in MeOH at room temperature. The expected *N*-heteroarylated 1*H*-(benz)imidazoles were obtained in high to excellent yields from both electron-rich and electron-deficient *B*-heteroarylboronic acid derivatives giving the best yields in case of *1*-heteroaryl-1*H*-benzimidazoles. We were able to use the more stable 2-heteroaryl-4,4,5,5-tetramethyl-1,3,2-dioxaborolanes as starting materials. To the best of our knowledge, this is the first time that their utilization was described in this methodology.

A limitation is that, under these conditions, no product was formed when *B*-(benzo)thien-2-yl-and *B*-(benzo)furan-2-ylboronic acids or their corresponding 4,4,5,5-tetramethyl-1,3,2-diaxoborolane were used.

This work was supported by the *Foundation for Science and Technology* (*FCT*), Portugal, through the Portuguese NMR network (*Bruker 400*) and by the *FCT* and *FEDER* (= ERDF = *European Regional Development Fund*) through the research unit *Centro de Química/UM* project FCOMP-01-0124-FEDER-022716 (ref. FCT PEst-C/QUI/UI0686/2011) and through the postdoctoral grant attributed to *A. Begouin* (SFRH/BPD/36753/2007) which is also financed by the *FSE* (= *ESF* = *European Social Fund*) and *POPH* (*Operational Programme of Human Potential*).

Experimental Part

General. Column chromatography (CC): *Macherey–Nagel* silica gel (SiO_2; 230–400 mesh); solvent gradient from neat petroleum ether (40–60°) to Et_2O/petroleum ether (40–60°), in steps of 10% of Et_2O each time until the isolation of the products; the most polar products were eluted with neat Et_2O, mixtures of Et_2O/AcOEt, or neat AcOEt. M.p.: *Stuart SMP3*; uncorrected. IR Spectra: *Bomem-FTLA-2000-104*; nujol mulls unless stated otherwise; $\tilde{\nu}$ in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: *Varian Unity Plus* at 300 and 75.4 MHz, resp., or *Bruker Avance III* at 400 and 100.6 MHz, resp; δ in ppm rel. to Me_4Si as internal standard, *J* in Hz., 2D ^1H,^{13}C correlations for the assignment of some signals (HMSC, HMBC). EI- and HR-MS: performed by the mass spectrometry service of the University of Vigo, Spain; in *m*/*z* (rel. %).

N-*Heteroarylation of 1*H-*(Benz)imidazole: General Procedure.* Cu_2O (5.5 mol-%) was added to a mixture of 1*H*-(benz)imidazole (1.2 equiv.) and *B*-heteroarylboronic acid (1.0 equiv.) or 2-heteroaryl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane in MeOH (3 ml) at r.t., and the mixture was stirred for several hours (*Table 1*, *Scheme 2*, and *Table 2*) under air. After completion of the reaction (TLC monitoring), $CHCl_3$ was added and the solvents were evaporated. The resulting oil was submitted to CC (silica gel) to give the corresponding product. See *Tables 1* and *2*.

*1-(Benzo[*b*]thien-3-yl)-1*H-*benzimidazole* (**1**) [15]: From *B*-benzo[*b*]thien-3-ylboronic acid (100 mg, 0.562 mmol) and 1*H*-benzimidazole (80.0 mg, 0.674 mmol). CC (50% Et_2O/petroleum ether): **1** (130 mg, 92%) Yellow pale oil. ^1H-NMR (400 MHz, $CDCl_3$): 7.30–7.44 (*m*, 4 H); 7.48–7.55 (*m*, 2 H); 7.62 (*s*, H–C(2′)); 7.93–7.99 (*m*, 2 H); 8.17 (*s*, H–C(2)).

*1-(Benzo[*b*]thien-3-yl)-1*H-*imidazole* (**2**) [16]: From *B*-benzo[*b*]thien-3-ylboronic acid (100 mg, 0.562 mmol) and 1*H*-imidazole (46.0 mg, 0.674 mmol). CC (50% Et_2O/petroleum ether): **2** (89.0 mg, 79%) Yellow pale oil. ^1H-NMR (400 MHz, $CDCl_3$): 7.33 (br. *s*, H–C(4), H–C(5)); 7.43–7.49 (*m*, 3 H); 7.67–7.71 (*m*, 1 H); 7.86 (br. *s*, H–C(2)); 7.88–7.94 (*m*, 1 H).

*1-(Thien-3-yl)-1*H-*benzimidazole* (**3**) [11b]: From *B*-3-thienylboronic acid (100 mg, 0.782 mmol) and 1*H*-benzimidazole (111 mg, 0.938 mmol). CC (60 to 80% Et_2O/petroleum ether): **3** (143 mg, 91%) Yellow oil. ^1H-NMR (300 MHz, $CDCl_3$): 7.26–7.38 (*m*, 4 H); 7.30–7.36 (*m*, 2 H); 7.49–7.54 (*m*, 2 H); 7.84–7.89 (*m*, 1 H); 8.09 (*s*, H–C(2)).

*1-(3-Thienyl)-1*H-*imidazole* (**4**) [11b]. From *B*-3-thienylboronic acid (100 mg, 0.782 mmol) and 1*H*-imidazole (73.0 mg, 0.938 mmol). CC (neat Et_2O to 30% AcOEt/Et_2O): **4** (90.0 mg, 77%) Yellow pale

solid. Recrystallization from Et_2O/petroleum ether gave yellow pale crystals. M.p. 87–89°. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.10–7.12 (*m*, 2 H); 7.14–7.16 (*m*, 1 H); 7.19 (br. *s*, H–C(4) or H–C(5)); 7.35–7.37 (*m*, 1 H); 7.77 (br. *s*, H–C(2)).

*1-(Dibenzothien-4-yl)-1*H-*benzimidazole* (**5**): From *B*-dibenzothien-4-ylboronic acid (100 mg, 0.438 mmol) and 1*H*-benzimidazole (62.0 mg, 0.526 mmol). CC (neat Et_2O): **5** (133 mg, 100%) Off-white solid. Recrystallization from Et_2O/petroleum ether gave off-white crystals. M.p. 136–138°. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.31–7.42 (*m*, 3 H); 7.49–7.57 (*m*, 3 H); 7.65 (*t*, *J* = 8.0, 1 H); 7.80–7.82 (*m*, 1 H); 7.97 (br. *d*, *J* = 8.0, 1 H); 8.23–8.25 (*m*, 1 H); 8.28–8.31 (*m*, H–C(2), 1 arom. H). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 111.00 (CH); 120.56 (CH); 121.81 (CH); 122.03 (CH); 122.89 (CH); 123.09 (CH); 123.68 (CH); 124.06 (CH); 124.98 (CH); 125.55 (CH); 127.67 (CH); 130.87 (C); 133.56 (C); 135.18 (C); 136.35 (C); 138.12 (C); 139.00 (C); 142.20 (C(2)); 143.33 (C). EI-MS: 302.07 (6), 301.08 (21), 300.07 (100, M^+), 299.07 (13), 299.07 (5), 272.05 (6), 171.03 (6). HR-MS: 300.0722 (M^+, $C_{19}H_{12}N_2S^+$; calc. 300.0721).

*1-(Dibenzothien-4-yl)-1*H-*imidazole* (**6**): From *B*-dibenzothien-4-ylboronic acid (100 mg, 0.438 mmol) and 1*H*-imidazole (36.0 mg, 0.526 mmol). CC (neat Et_2O): **6** (87.0 mg, 80%) Brown solid. Recrystallization from Et_2O/petroleum ether gave beige crystals. M.p. 120–121°. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.35 (br. *s*, H–C(4) or H–C(5)); 7.43 (br. *d*, *J* = 8.0, 1 H); 7.49 (br. *s*, H–C(4) or H–C(5)); 7.50–7.54 (*m*, 2 H); 7.57 (*t*, *J* = 8.0, 1 H); 7.84–7.88 (*m*, 1 H), 8.00 (br. *s*, H–C(2)); 8.19–8.21 (*m*, 2 H). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 119.37 (C(4) or C(5)); 121.17 (CH); 122.02 (CH); 122.07 (CH); 122.84 (CH); 125.00 (CH); 125.51 (CH); 127.64 (CH); 130.17 (C(4) or C(5)); 132.62 (C); 134.50 (C); 135.21 (C); 136.82 (C(2)); 137.98 (C); 138.99 (C). EI-MS: 252.06 (5), 251.06 (18), 250.06 (100, M^+), 249.05 (33), 223.04 (30), 222.04 (20), 210.04 (13), 196.03 (20), 183.03 (10), 152.06 (15), 139.06 (31). HR-MS: 250.0567 (M^+, $C_{15}H_{10}N_2S^+$; calc. 250.0565).

*1-(Thianthren-1-yl)-1*H-*benzimidazole* (**7**): From *B*-thianthren-1-ylboronic acid (100 mg, 0.384 mmol) and 1*H*-benzimidazole (62.0 mg, 0.526 mmol). CC (60% Et_2O/petroleum ether to neat Et_2O): **7** (131 mg, 100%) Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.17–7.21 (*m*, 2 H); 7.25–7.42 (*m*, 6 H); 7.50–7.52 (*m*, 1 H); 7.65 (*dd*, *J* = 7.6, 1.6, 1 H); 7.95 (br. *d*, *J* = 8.0, 1 H); 8.06 (*s*, H–C(2)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 110.56 (CH); 120.44 (CH); 122.80 (CH); 123.67 (CH); 126.45 (CH); 128.00 (CH); 128.13 (CH); 128.21 (CH); 128.66 (CH); 129.00 (CH); 129.41 (CH); 133.96 (C); 134.41 (C); 134.51 (C); 135.40 (C); 138.09 (C); 142.80 (C(2)); 143.16 (C). EI-MS: 334.05 (7), 333.05 (17), 332.04 (100, M^+), 331.04 (26), 300.07 (10), 299.06 (17), 298.06 (11). HR-MS: 332.0447 (M^+, $C_{19}H_{12}N_2S_2^+$; calc. 332.0442).

*1-(Thianthren-1-yl)-1*H-*imidazole* (**8**): From *B*-thianthren-1-ylboronic acid (100 mg, 0.384 mmol) and 1*H*-imidazole (36.0 mg, 0.526 mmol). CC (60% Et_2O/petroleum ether to neat Et_2O): **8** (90.0 mg, 83%) Yellow pale solid. Recrystallization from ether/ petroleum ether gave off-white crystals. M.p. 105–106°. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.17 (br. *s*, H–C(4) or H–C(5)); 7.20–7.35 (*m*, 5 H); 7.39 (*dd*, *J* = 7.6, 1.6, 1 H); 7.49 (*dd*, *J* = 7.6, 1.2, 1 H); 7.57 (*dd*, *J* = 7.6, 1.2, 1 H); 7.72 (br. *s*, H–C(2)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 120.86 (C(4) or C(5)); 125.55 (CH); 127.85 (CH); 127.99 (CH); 128.26 (CH); 128.68 (CH); 128.98 (CH); 129.15 (CH); 129.49 (C(4) or C(5)); 133.39 (C); 134.08 (C); 135.46 (C); 136.22 (C); 137.54 (C); 137.66 (C(2)). EI-MS: 284.03 (8), 283.03 (14), 282.03 (100, M^+), 281.02 (11), 223.04 (11), 222.04 (12), 210.04 (11), 209.03 (11), 171.03 (16). HR-MS: 282.0290 (M^+, $C_{15}H_{10}N_2S_2^+$; calc. 282.0285).

*1-(Furan-3-yl)-1*H-*benzimidazole* (**9**) [11b]: From *B*-furan-3-ylboronic acid (100 mg, 0.894 mmol) and 1*H*-benzimidazole (127 mg, 1.07 mmol). CC (neat Et_2O): **9** (130 mg, 79%) Ochre solid. Recrystallization from Et_2O/petroleum ether gave beige crystals. M.p. 80–82°. From 2-(furan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (100 mg, 0.515 mmol) and 1*H*-benzimidazole (73.0 mg, 0.618 mmol) after CC: **9** (50.0 mg, 53%).

*1-(Furan-3-yl)-1*H-*imidazole* (**10**) [11b]. From *B*-furan-3-ylboronic acid (100 mg, 0.894 mmol) and 1*H*-imidazole (73.0 mg, 1.07 mmol). CC (neat Et_2O): **10** (85.0 mg, 71%) Yellow pale oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 6.58–6.59 (*m*, 1 H); 7.14 (br. *s*, H–C(4) or H–C(5)); 7.19 (br. *s*, H–C(4) or H–C(5)); 7.47–7.48 (*m*, 1 H); 7.66–7.67 (*m*, 1 H); 7.73 (br. *s*, H–C(2)). From 2-(furan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (100 mg, 0.515 mmol) and 1*H*-imidazole (42.0 mg, 0.618 mmol) after CC: **10** (35.0 mg, 51%).

*1-(Dibenzofuran-4-yl)-1*H*-benzimidazole* (**11**): From *B*-dibenzofuran-4-ylboronic acid (100 mg, 0.472 mmol) and 1*H*-benzimidazole (67.0 mg, 0.566 mmol). CC (neat petroleum ether to 80% Et_2O/petroleum ether): **11** (131 mg, 98%) Yellow pale solid. Recrystallization from Et_2O/petroleum ether gave yellow crystals. M.p. 123–124°. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.34–7.45 (*m*, 3 H); 7.50–7.59 (*m*, 4 H); 7.65 (*dd*, *J* = 7.8, 1.0, 1 H); 7.97 (br. *d*, *J* = 7.2, 1 H); 8.04–8.07 (*m*, 2 H); 8.43 (*s*, H–C(2)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 110.89 (CH); 112.14 (CH); 120.32 (CH); 120.61 (CH); 121.00 (CH); 121.19 (C); 122.74 (CH); 122.92 (CH); 123.52 (CH); 123.58 (CH); 123.69 (C); 123.75 (CH); 126.86 (C); 128.15 (CH); 133.90 (C); 143.09 (C(2)); 143.69 (C); 149.16 (C); 156.27 (C). EI-MS: 285.10 (19), 284.10 (100, M^+), 283.09 (11), 256.08 (6), 255.09 (8). HR-MS: 284.0946 (M^+, $C_{19}H_{12}N_2O^+$; calc. 284.0950).

*1-(Dibenzofuran-4-yl)-1*H*- imidazole* (**12**). From *B*-dibenzofuran-4-ylboronic acid (100 mg, 0.472 mmol) and 1*H*-imidazole (39.0 mg, 0.566 mmol). CC (40% Et_2O/petroleum ether to neat Et_2O): **12** (84.0 mg, 76%) Yellow pale solid. Recrystallization from Et_2O/petroleum ether gave off-white crystals. M.p. 87–89°. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.33 (br. *s*, H–C(4) or H–C(5)); 7.40–7.46 (*m*, 2 H); 7.49–7.56 (*m*, 2 H); 7.62–7.64 (*m*, 2 H); 7.94 (br. *d*, *J* = 7.4, 1 H); 8.00 (br. *d*, *J* = 8.0, 1 H); 8.23 (*s*, H–C(2)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 112.05 (CH); 118.99 (H–C(4) or H–C(5)); 119.35 (CH), 119.72 (CH); 120.96 (CH); 122.54 (C); 123.50 (CH); 123.58 (CH); 126.76 (C); 128.12 (CH); 129.79 (H–C(4) or H–C(5)); 136.92 (C(2)); 147.27 (C); 156.21 (C). EI-MS: 235.09 (15), 234.08 (100, M^+), 207.07 (57), 206.06 (11), 194.06 (19), 180.06 (32), 152.06 (16), 139.05 (38). HR-MS: 234.0799 (M^+, $C_{15}H_{10}N_2O^+$; calc. 234.0793).

*3-(1*H*-Benzimidazol-1-yl)quinoline* (**13**). From 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)quinoline (100 mg, 0.392 mmol) and 1*H*-benzimidazole (56.0 mg, 0.470 mmol). CC (neat Et_2O to neat AcOEt): **13** (78.0 mg, 81%) Yellow pale solid. Recrystallization from Et_2O/petroleum ether gave off-white crystals. M.p. 142–144°. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.34–7.39 (*m*, 2 H); 7.54–7.56 (*m*, 1 H); 7.64–7.68 (*m*, 1 H); 7.79–7.83 (*m*, 1 H); 7.90–7.93 (*m*, 2 H); 8.21–8.25 (*m*, 3 H); 9.10 (*d*, *J* = 2.4, H–C(2). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 109.93 (CH); 120.80 (CH); 123.20 (CH); 124.14 (CH); 127.65 (C); 127.70 (CH); 128.05 (CH); 129.54 (CH); 129.58 (CH); 129.74 (C); 130.25 (CH); 133.74 (C); 142.05 (CH); 143.97 (C); 146.27 (C(2)); 147.24 (C). EI-MS: 246.10 (15), 245.10 (100, M^+), 244.09 (37), 219.09 (4), 218.08 (9), 217.08 (5), 190.07 (7), 117.06 (10), 101.04 (9). HR-MS: 245.0956 (M^+, $C_{16}H_{11}N_3^+$; calc. 245.0953).

*3-(1*H*-Imidazol-1-yl)quinoline* (**14**): From 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)quinoline (100 mg, 0.391 mmol) and 1 H-imidazole (32.0 mg, 0.470 mmol). CC (50% AcOEt/Et_2O to neat AcOEt): **14** (59.0 mg, 78%) Beige solid. Recrystallization from Et_2O/petroleum ether gave beige crystals. M.p. 141–143°. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.36 (br. *s*, H–C(4′) or H–C(5′)); 7.47 (br. *s*, H–C(4′) or H–C(5′)); 7.64–7.67 (*m*, 1 H); 7.76–7.81 (*m*, 1 H); 7.89 (*d*, *J* = 8.0, 1 H); 8.05 (br. *s*, H–C(2′)); 8.14–8.19 (*m*, 2 H); 9.04 (*d*, *J* = 2.4, H–C(2)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 118.72 (C(4′) or C(5′)); 126.86 (CH); 127.56 (C); 127.69 (CH); 128.17 (CH); 129.54 (CH); 130.06 (CH); 130.76 (C); 131.16 (C(4′) or C(5′)); 136.06 (C(2′)); 144.50 (C(2)); 147.17 (C). EI-MS: 196.08 (11), 195.07 (100, M^+), 194.07 (13), 168.06 (79), 142.06 (12), 141.06 (44), 140.05 (15), 128.05 (14), 114.04 (18), 101.04 (24). HR-MS: 195.0800 (M^+, $C_{12}H_9N_3^+$; calc. 195.0796).

*4-(1*H*-Benzimidazol-1-yl)isoquinoline* (**15**). From 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)isoquinoline (100 mg, 0.391 mmol) and 1*H*-benzimidazole (56.0 mg, 0.470 mmol). CC (50% Et_2O/petroleum ether to neat Et_2O): **15** (75.0 mg, 78%) Yellow pale solid. Recrystallization from Et_2O/petroleum ether gave off-white crystals. M.p. 141–143°. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.12 (*d*, *J* = 8.0, 1 H); 7.29–7.31 (*m*, 1 H); 7.38 (*t*, *J* = 7.6, 1 H); 7.50 (*d*, *J* = 7.6, 1 H); 7.69–7.77 (*m*, 2 H); 7.96 (*d*, *J* = 8.0, 1 H); 8.17–8.19 (*m*, H–C(2′), 1 arom. H); 8.65 (*s*, H–C(3) or H–C(1)); 9.43 (*s*, H–C(3) or H–C(1)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 110.53 (CH); 120.53 (CH); 121.53 (CH); 123.08 (CH); 123.99 (CH); 127.71 (C); 128.11 (CH); 128.54 (CH); 129.05 (C); 132.03 (CH); 132.31 (C); 135.34 (C); 137.61 (C); 140.99 (C(3) or C(1)); 143.32 (CH(2′); 153.71 (C(1) or C(3)). EI-MS: 246.10 (15), 245.10 (100, M^+), 244.09 (49), 219.09 (8), 218.08 (68), 217.08 (11), 190.06 (13), 118.05 (29). HR-MS: 245.0956 (M^+, $C_{16}H_{11}N_3^+$; calc. 245.0953).

*4-(1*H*-Imidazol-1-yl)isoquinoline* (**16**): From 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)isoquinoline (100 mg, 0.391 mmol) and 1*H*-imidazole (32.0 mg, 0.470 mmol). CC (50% AcOEt/Et_2O to neat AcOEt): **16** (64.0 mg, 84%) Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.26 (br. *s*, H–C(4′) or H–C(5′));

7.31 (br. *s*, H–C(4′) or H–C(5′)); 7.64 – 7.78 (*m*, H–C(2′) and 3 arom. H); 8.08 (br. *d*, *J* = 7.6, 1 H); 8.50 (*s*, H–C(3) or H–C(1)); 9.30 (*s*, H–C(1) or H–C(3)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 121.13 (CH); 121.40 (C(4′) or C(5′)); 127.84 (CH); 128.31 (CH); 128.73 (C); 129.13 (C); 130.04 (C(4′) or C(5′)); 131.84 (C); 131.99 (CH); 138.14 (C(2′)); 139.51 (C(3) or C(1)); 153.20 (C(1) or C(3)). EI-MS: 196.08 (16), 195.08 (95, M^+), 194.07 (11), 169.07 (13), 168.07 (100, $[M-27]^+$), 167.06 (35), 140.05 (22). HR-MS: 195.0801 (M^+, $C_{12}H_9N_3^+$; calc. 195.0796).

*1-(6-Fluoropyridin-3-yl)-1*H*-benzimidazole* (**17**). From 2-fluoro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (80 mg, 0.359 mmol) and 1*H*-benzimidazole (51.0 mg, 0.430 mmol). CC (neat Et_2O to 20% AcOEt/Et_2O): **17** (50.0 mg, 54%) Yellow solid. Recrystallization from ether/petroleum ether gave yellow pale crystals. M.p. 141 – 143°. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.20 (*dd*, *J* = 8.6, 3.4, H–C(5′)); 7.36 – 7.41 (*m*, 2 H); 7.44 – 7.46 (*m*, 1 H); 7.90 – 7.92 (*m*, 1 H); 7.96 – 8.01 (*m*, H–C(4′)); 8.11 (br. *s*, 1 H); 8.45 – 8.46 (*m*, H–C(2′)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 109.71 (CH); 110.96 (*d*, *J* = 39.2, C(5′)); 120.94 (CH); 123.37 (CH); 124.36 (CH); 131.13 (C(3′)); 133.91 (C); 137.09 (*d*, *J* = 8, C(4′)); 141.87 (C(2)); 143.35 (*d*, *J* = 16, C(2′)); 143.99 (C); 162.49 (*d*, *J* = 242, C–F). EI-MS: 214.07 (13), 213.07 (100, M^+), 212.07 (15), 186.06 (15). HR-MS: 213.0703 (M^+, $C_{12}H_8F^+N_3$; calc. 213.0702).

*2-Fluoro-5-(1*H*-imidazol-1-yl)pyridine* (**18**): From 2-fluoro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (80 mg, 0.359 mmol) and 1*H*-imidazole (29.0 mg, 0.430 mmol). CC (neat Et_2O to neat AcOEt): **18** (25.0 mg, 43%) Yellow pale solid. Recrystallization from Et_2O/petroleum ether gave off-white crystals. M.p. 88 – 90°. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.10 (*dd*, *J* = 8.8, 3.2, H–C(5′)); 7.39 (br. *s*, H–C(4), H–C(5)); 7.84 – 7.88 (*m*, H–C(4′)); 7.96 (br. *s*, H–C(2)); 8.34 – 8.35 (*m*, H–C(2′)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 110.70 (*d*, *J* = 39, C(5′)); 131.45 (CH); 132.36 (C(3′)); 134.82 (*d*, *J* = 8, C(4′)); 135.05 (CH); 135.78 (CH); 140.88 (*d*, *J* = 16, C(2′)); 162.24 (*d*, *J* = 241, C–F). EI-MS: 164.06 (11), 163.05 (100, M^+), 162.05 (4), 136.04 (38,), 109.03 (46), 96.03 (26). HR-MS: 163.0545 (M^+, $C_8H_6F^+N_3$; calc. 163.0546).

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