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Synthesis of Benzimidazoles through Palladium-Catalyzed Amination of 2-Iodobenzimines with Diaziridinone

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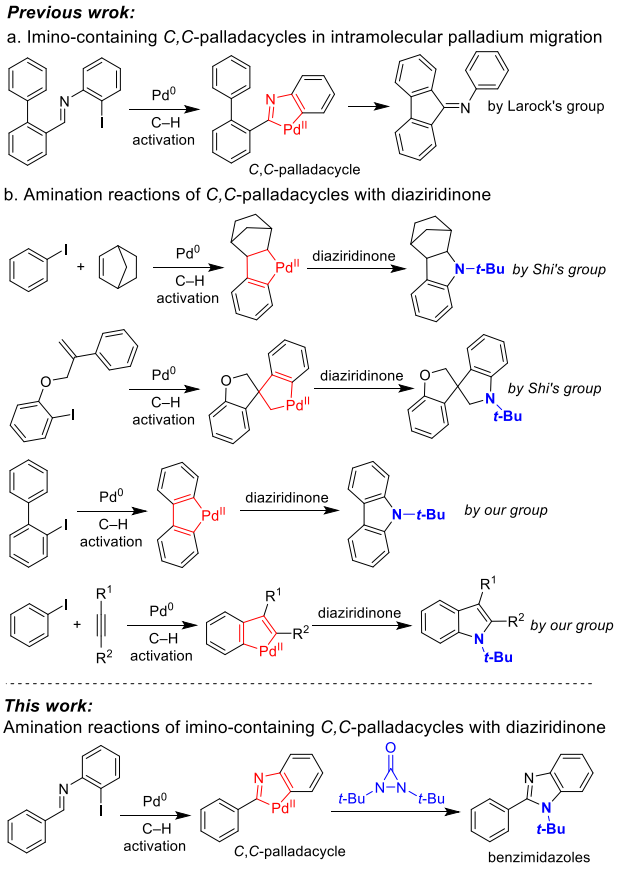
Abstract. An efficient approach for the synthesis of benzimidazoles has been developed through the Pd-catalyzed amination of 2-iodobenzimines with diaziridinone. A wide range of 2-(hetero)aryl benzimidazloes are synthesized in good to excellent yields. The reactions likely involve *C,C*-palladacycles derived from 2-iodobenzimines as the key intermediate, and the palladacycles reacted with diaziridinone to form benzimidazoles.

Keywords: Palladacycles; C–H activation; Amination; Palladium; Benzimidazole.

Introduction

Benzimidazoles are ubiquitous structural motifs in naturally occurring compounds.[1] More importantly, this class of *N*-containing heterocycles may exhibit remarkable biological activities such as anticancer and antimicrobial activity.[2] Consequently, benzimidazoles are popular and crucial core structures in drug discovery and have successfully been developed into pharmaceuticals.[3] Furthermore, they have also found extensive applications in materials science.[4] It is not surprising that developing synthetic methods for benzimidazoles has been the subject of intensive research, and a number of synthetic reactions have been developed.[5] Traditionally, benzimidazoles are synthesized by the condensation of 1, 2-diaminoarenes with carbonyl derivatives.[6] A strategy involving transition-metal-catalyzed C–N bond formation represents a relatively modern approach.[7]

C,C-palladacycles are an important class of metallacycles. *C,C*-palladacycles consist of two C-Pd bonds, and the two C–Pd bonds can be utilized to develop new transformations.[8] A variety of *C,C*-palladacycles are available, including those consisting of a C(sp^2)–Pd–C(sp^2) or C(sp^2)–Pd–C(sp^3) bonding motif, and quite a few novel reactions have been developed by capitalizing on the unique reactivity and structures of these palladacycles.[9] Our group has been interested in *C,C*-palladacycles, and developed some synthetically useful reactions through intermolecular functionalization of this unique class of palladacycles recently.[10]



Scheme 1. Reactions of Imino-Containing *C,C*-Palladacycles Derived from 2-Iodobenzimines and Amination Reactions of *C,C*-Palladacycles with Di-*tert*-Butyldiaziridinone .

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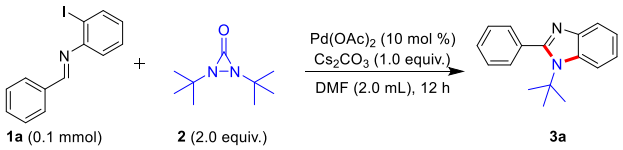
The majority of the current *C,C*-palladacycles consist of two aryl C-Pd bonds. It is desirable to study other types of *C,C*-palladacycles and develop their reactions. In 2007, the Larock group reported a novel aryl to imidoyl palladium migration reaction of 2-iodobenzimine derivatives (**Scheme 1**).[11a] This reaction involved a five-membered *C,C*-palladacycle as the intermediate. This palladacycle contains an imino moiety and represents a new class of *C,C*-palladacycles, and can be utilized to develop synthetically useful reactions, in particular for *N*-containing heterocycles. However, this *C,C*-palladacycle has not been exploited to develop other organic reactions.[11b, c, d] On the other hand, the Shi group demonstrated that diaziridinone exhibits high reactivity towards *C,C*-palladacycles (**Scheme 1**).[12a, b] Inspired by this pioneering work, our group developed amination reactions of *C,C*-palladacycles derived from 2-iodobiphenyls or formed through the reaction of aryl iodides and alkynes (**Scheme 1**).[12c, d] We envisioned that diaziridinone might also react with the *C,C*-palladacycles derived from 2-iodobenzimines. Herein, we report a protocol for the Pd-catalyzed reaction of 2-iodobenzimines with diaziridinone, which represents a new approach for the construction of benzimidazoles.

Results and Discussion

We commenced our studies by investigating the reaction of 2-iodobenzimine **1a** with diaziridinone **2**. As shown in **Table 1**, in the presence of KOAc as a base, the desired benzimidazole **3a** was formed in 14% yield (entry 1), and a yield of 20% was obtained by using 1 equivalent of Cs_2CO_3 (entry 2). Gratefully, the yield was dramatically improved to 72% when a combination of KOAc and Cs_2CO_3 was added (entry 3). Replacing KOAc with KOPiv resulted in a slightly higher yield (entry 4), and the yield was further enhanced to 84% by elevating the reaction temperature (entry 5). Unexpectedly, a yield as high as 95% was obtained when 1 equivalent of KOPiv was used (entry 6). Further reducing the equivalents of the base led to a lower yield (entry 7). The exact roles of KOPiv and Cs_2CO_3 remain to be investigated. They should be able to promote the generation of the active Pd(0) species and C−H activation.[12c][13] Notably, the yield remained to be excellent even using 1.5 equivalents of **2** (entry 8). However, the yield decreased when one equivalent of **2** was used (entry 9). The desired product was still obtained in 85% yield in the presence of 5 mol% $Pd(OAc)_2$ (entry 10). The reaction was completed in 3 hours and the excellent yield was still obtained (entry 11).

Table 1. Optimization of Reaction Conditions.



1a (0.1 mmol) **2** (2.0 equiv.) **3a**

entry	Base (equiv.)	temperature (°C)	yield (%)[a]
1[b]	KOAc (2.0)	110	14
2	\	110	20
3	KOAc (2.0)	110	72
4	KOPiv (2.0)	110	78
5	KOPiv (2.0)	135	84
6	KOPiv (1.0)	135	95
7	KOPiv (0.5)	135	77
8[c]	KOPiv (1.0)	135	95
9[d]	KOPiv (1.0)	135	73
10[e]	KOPiv (1.0)	135	83
11[c, f]	KOPiv (1.0)	135	94 (91[g])

[a] The yields were determined by ^1H NMR analysis of crude reaction mixture using CH_2Br_2 as the internal standard.
[b] No Cs_2CO_3.
[c] 1.5 equiv. of **1a**.
[d] 1.0 equiv. of **1a**.
[e] 5 mol % $Pd(OAc)_2$.
[f] 3 h.
[g] Isolated yield.

After developing an efficient protocol for the synthesis of benzimidazoles, we then explored its substrate scope towards a variety of 2-iodobenzimines. We first examined the compatibility of functional groups on the iodo-bearing benzene rings. As shown in **Table 2**, the electron-donating methyl and methoxy groups were compatible and the corresponding products were formed in excellent yields (**3b** and **3c**). The fluoro and chloro group were also well-tolerated (**3d** and **3e**). While the fluoro-substituted benzimidazole was formed in an excellent yield, the presence of a chloro group led to a moderate yield. As it has been reported that P(*o*-tol)$_3$ could promote the functionalization reaction of *C,C*-palladacycles obtained from aryl halides,[10d] we investigated the impact of the ligand on this amination reaction. Gratefully, a 76% yield was obtained by the addition of 20 mol% P(*o*-tol)$_3$ as a ligand. The substrates bearing a typical electron-withdrawing group such as trifluoromethyl, ester, and cyano were also suitable, albeit in low yields (**3f-3h**). Likewise, the yields could be improved by using ligand P(*o*-tol)$_3$. Benzimines bearing a methyl group on the positions *ortho* or *meta* to the benzylideneamino group also underwent the amination reaction, and the yields were high (**3i** and **3j**).

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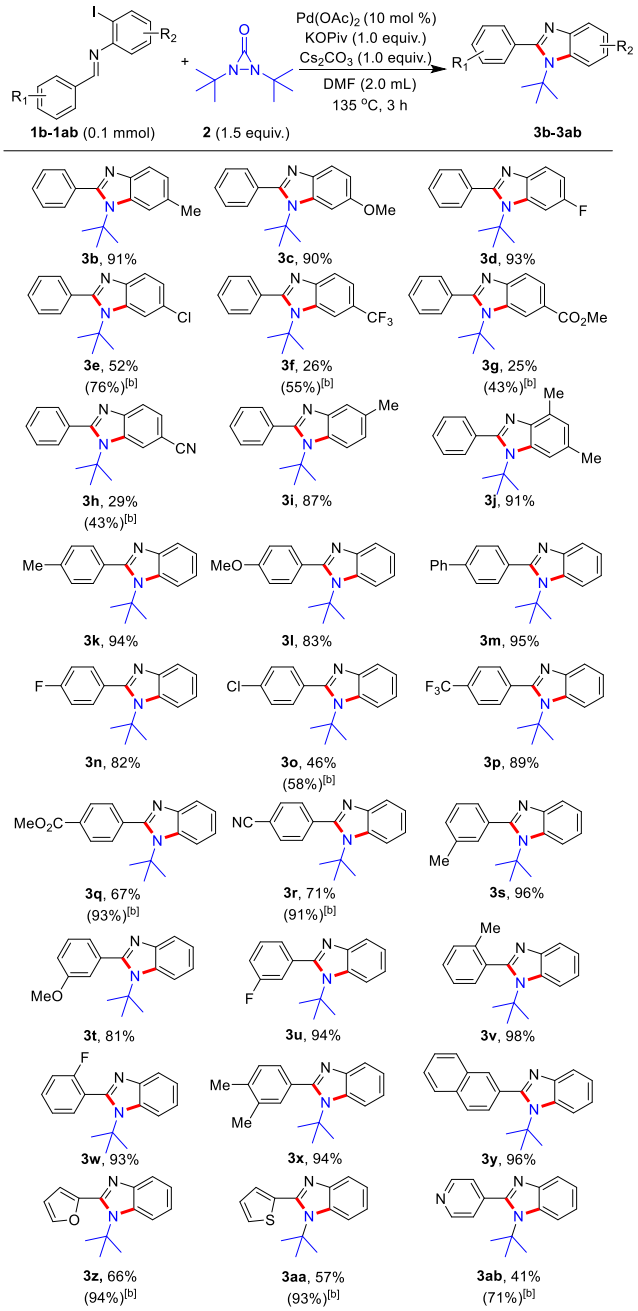
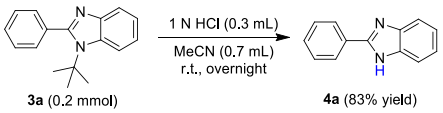
Table 2. Substrate Scope.[a]



[a] Isolated yield.
[b] 20 mol % P(*o*-tol)$_3$ was added.

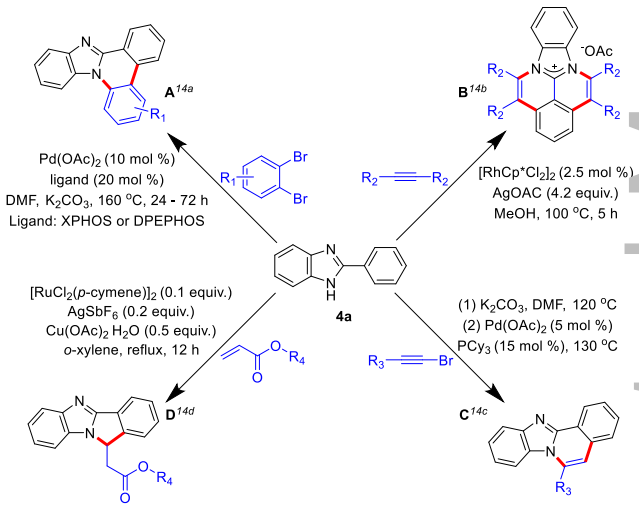
Next, we investigated the performance of substituents on the other benzene ring. A range of substituents on the *para* positions were compatible (**3k**-**3r**). The yields were good or excellent for most of the substituents. Although the ester and cyano groups gave lower yields, the yields could be enhanced to over 90% by the addition of P(*o*-tol)$_3$ (**3q** and **3r**). The presence of substituents on the *meta* or *ortho* positions did not affect the high efficiency of the benzimidazole-forming reaction (**3s**-**3w**), and disubstituted derivatives also exhibited excellent reactivity (**3x** and **3y**). Notably, the substrates containing an aromatic heterocycle including furan, thiophene, and pyridine were also suitable (**3z**-**3ab**). The corresponding benzimidazoles were formed in good or excellent yields in the presence of P(*o*-tol)$_3$.

The *tert*-butyl group of the resulting benzimidazole products could be readily removed under acidic conditions (**Scheme 2**).[14] The resulting free amine can be manipulated, which allows easy access to a variety of 1-substituted benzimidazole derivatives.



Scheme 2. Deprotection of the Benzimidazole Products.

Our reaction forms 2-arylbenzimidazoles as the products. Notably, it has been reported that 2-arylbenzimidazoles can be transformed into diverse polycyclic heterocycles that are pharmacologically important or have potential applications in materials science. As shown in **Scheme 3**, 2-phenyl benzimidazole **4a** can react with *o*-dibromobenzene to form *N*-heteroaryl-fused phenanthridines (**A**).[15a] **4a** can also react with alkynes, and the reaction yielded N-doped benzo-[*cd*]fluoranthenium salts (**B**)[15b] or benzimidazole-fused isoquinolines (**C**).[15c] Furthermore, benzoimidazoisoindoles can be easily accessed through the reaction of 2-arylbenzimidazoles with alkenes (**D**).[15d]



Scheme 3. Transformation of 2-Arylbenzimidazoles.

Next, we investigated the kinetic isotope effect in this amination reaction. Deuterated 2-iodobenzimine **1a-D$_6$** was synthesized. When a mixture of **1a** and **1a-D$_6$** in a ratio of 1:1 was subjected to the standard conditions and the reaction was stopped in 15 minutes, the equal quantities of **3a** and **3a-D$_6$** were formed (**Scheme 4**). Therefore, the intermolecular KIE value was 1.0. Furthermore, parallel reactions of **1a** and **1a-D$_6$** were also carried out, and the KIE value was 1.1(**Scheme 4**). These results indicate that C−H bond cleavage was not the turnover-limiting step.

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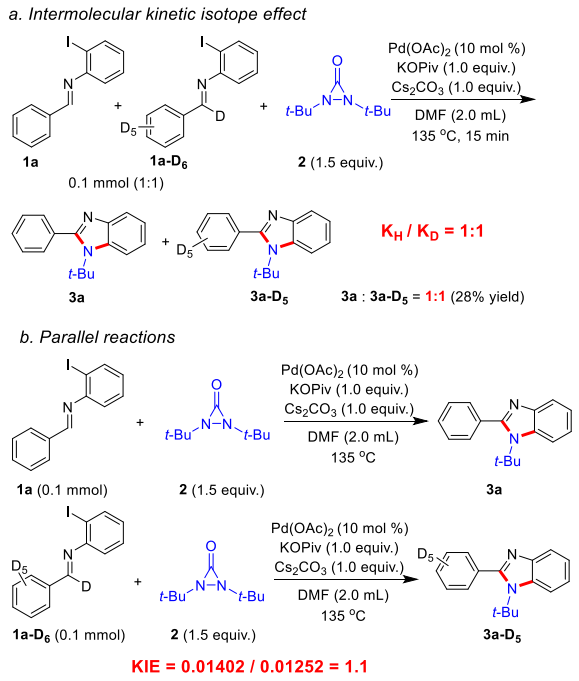
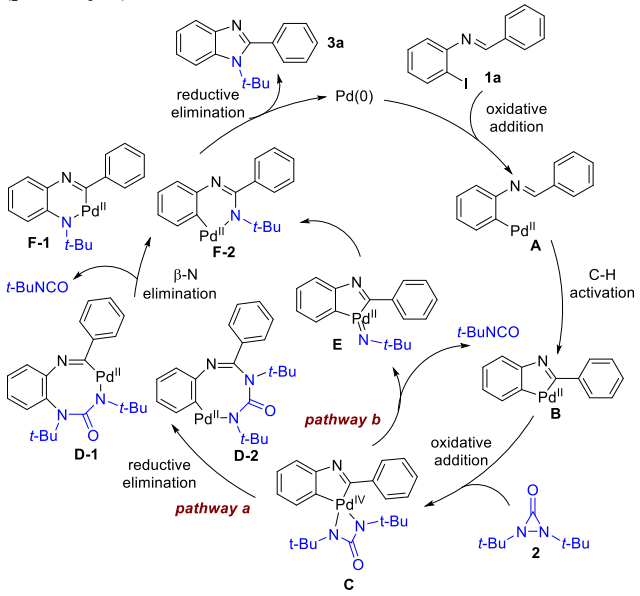


Scheme 4. Kinetic Isotope Effect.

On the basis of the products formed in the reaction and the previous reports,[11, 12] we proposed a tentative mechanism for the benzimidazole-forming reaction. As shown in **Scheme 5**, the catalytic cycle starts with the oxidative addition of 2-iodobenzimine to Pd(0) to generate Pd(II) species **A**. The subsequent intramolecular C−H activation affords palladacycle **B**. Next, **B** inserts into the N−N bond of diaziridinone through oxidative addition to provide pallada(IV)cycle **C**. **C** then undergoes reductive elimination to give intermediate **D-1** or **D-2** (pathway a). The subsequent β-*N* elimination and reductive elimination yield product **3a** and release Pd(0) catalyst. It should be mentioned that a Pd−nitrene pathway cannot be ruled out (pathway b).



Scheme 5. Proposed Mechanism.

Conclusion

In conclusion, we have developed a new protocol for the synthesis of benzimidazoles starting from 2-iodobenzimines and diaziridinones. *C,C*-Palladacycles that are obtained through intramolecular C−H activation of 2-iodobenzimines act as the key intermediates. The palladacycles are aminated with diaziridinone efficiently to yield benzimidazoles. The reaction features broad substrate scope and high yields. The resulting 2-(hetero)aryl benzimidazloes can be transformed into biologically important diverse polycyclic heterocycles.

Experimental Section

General Procedure for the Synthesis of Benzimidazoles. A 25 mL Schlenk-type tube (with a Teflon screw cap and a side arm) equipped with a magnetic stir bar was charged with $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), Cs_2CO_3 (32.6 mg, 0.1 mmol), KOPiv (14.0 mg, 0.1 mmol), the corresponding substrate (0.1 mmol), di-*tert*-butyldiaziridinone (25.5 mg, 0.15 mmol) and DMF (2 mL). The reaction tube was evacuated and backfilled with nitrogen (5 times). The mixture was stirred at 135 °C for 3 hours. After cooling to room temperature, the reaction mixture was diluted with EtOAc (15 mL), washed with saturated NaCl solution (3 times), dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by preparative silica gel TLC with PE/EA to give the corresponding products.

1-(*tert*-Butyl)-2-phenyl-1H-benzo[d]imidazole (3a): White solid; Yield: 91% (22.7 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 – 7.77 (m, 1H), 7.75 – 7.71 (m, 1H), 7.49 (d, *J* = 6.9 Hz, 2H), 7.47 – 7.40 (m, 3H), 7.29 – 7.27 (m, 2H), 1.63 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.5, 143.2, 135.8, 134.9, 129.7, 129.0, 127.8, 122.0, 121.9, 120.2, 114.7, 58.9, 31.4. HRMS (ESI-TOF) m/z: calculated for $C_{17}H_{18}N_2Na^+$: 273.1362 $(M + Na)^+$, found: 273.1370.

1-(*tert*-Butyl)-6-methyl-2-phenyl-1H-benzo[d]imidazole (3b): White solid; Yield: 91% (24.1 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.1 Hz, 1H), 7.51 (s, 1H), 7.47 (d, *J* = 6.8 Hz, 2H), 7.44 – 7.39 (m, 3H), 7.10 (d, *J* = 8.1 Hz, 1H), 2.54 (s, 3H), 1.61 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.1, 141.4, 136.0, 135.1, 131.6, 129.7, 128.9, 127.7, 123.4, 119.6, 114.6, 58.7, 31.4, 22.2. HRMS (ESI-TOF) m/z: calculated for $C_{18}H_{20}N_2Na^+$: 287.1519 $(M + Na)^+$, found: 287.1525.

1-(*tert*-Butyl)-6-methoxy-2-phenyl-1H-benzo[d]imidazole (3c): White solid; Yield: 90% (25.2 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.7 Hz, 1H), 7.53 – 7.34 (m, 5H), 7.20 (s, 1H), 6.94 (d, *J* = 8.1 Hz, 1H), 3.91 (s, 3H), 1.60 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.5, 153.0, 138.0, 135.9, 135.4, 129.7, 128.9, 127.7, 120.3, 110.1, 99.6, 58.7, 56.1, 31.3. HRMS (ESI-TOF) m/z: calculated for $C_{18}H_{20}N_2NaO^+$:303.1468 $(M + Na)^+$, found: 303.1474.

1-(*tert*-Butyl)-6-fluoro-2-phenyl-1H-benzo[d]imidazole (3d): White solid; Yield: 93% (24.9 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 8.8, 5.4 Hz, 1H), 7.47 (d, *J* = 6.7 Hz, 2H), 7.45 – 7.39 (m, 4H), 7.03 (td, *J* = 9.1, 2.2 Hz, 1H), 1.59 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.7 (d, *J* = 236.8 Hz), 154.2 (d, *J* = 2.9 Hz), 139.6, 135.5, 134.7 (d, *J* = 12.9 Hz), 129.6, 129.1, 127.8, 120.6 (d, *J* = 10.3 Hz), 110.2 (d, *J* = 24.9 Hz), 101.3 (d, *J* = 28.7 Hz), 59.1, 31.3. HRMS (ESI-TOF) m/z: calculated for $C_{17}H_{17}FN_2Na^+$: 291.1268 (M + Na)$^+$, found: 291.1276.

1-(*tert*-Butyl)-6-chloro-2-phenyl-1H-benzo[d]imidazole (3e): White solid; Yield: 76% (21.6 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.69 (d, *J* = 8.5 Hz, 1H), 7.49 – 7.47 (m, 3H), 7.46 – 7.42 (m, 2H), 7.29 – 7.27 (m, 1H), 1.62 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.4, 141.8, 135.4, 135.3, 129.6, 129.2, 127.9, 127.6, 122.5, 120.8, 114.5, 59.3, 31.4. HRMS (ESI-TOF) m/z: calculated for $C_{17}H_{17}ClN_2Na^+$: 307.0972 (M + Na)$^+$, found: 307.0982.

1-(*tert*-Butyl)-2-phenyl-6-(trifluoromethyl)-1H-benzo[d]imidazole (3f): White solid; Yield: 55% (17.5 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.49 – 7.42 (m, 5H), 1.64 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.1, 145.4, 135.1, 134.3, 129.5, 129.4, 127.9, 124.9 (q, *J* = 270.9 Hz), 124.1 (q, *J* = 32.1 Hz), 120.5, 118.9 (q, *J* = 3.5 Hz), 112.1 (q, *J* = 4.4 Hz), 59.6, 31.5. HRMS (ESI-TOF) m/z: calculated for $C_{18}H_{17}F_3N_2Na^+$: 341.1236 (M + Na)$^+$, found: 341.1244.

Methyl 1-(*tert*-Butyl)-2-phenyl-1H-benzo[d]imidazole-6-carboxylate (3g): White solid; Yield: 43% (13.2 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.50 – 7.42 (m, 5H), 3.97 (s, 3H), 1.65 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.7, 156.3, 146.8, 135.2, 134.6, 129.5, 129.3, 127.9, 123.7, 123.3, 119.7, 117.0, 59.6, 52.2, 31.6. HRMS (ESI-TOF) m/z: calculated for $C_{19}H_{20}N_2NaO_2^+$: 331.1417 (M + Na)$^+$, found: 331.1422.

1-(*tert*-Butyl)-2-phenyl-1H-benzo[d]imidazole-6-carbonitrile (3h): White solid; Yield: 43% (11.8 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.82 (d, *J* = 8.3 Hz, 1H), 7.54 (d, *J* = 8.3 Hz, 1H), 7.52 – 7.41 (m, 5H), 1.63 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.0, 146.1, 134.6, 134.4, 129.6, 129.4, 128.0, 125.3, 121.1, 120.2, 119.4, 104.9, 59.9, 31.5. HRMS (ESI-TOF) m/z: calculated for $C_{18}H_{17}N_3Na^+$: 298.1315 (M + Na)$^+$, found: 298.1320.

1-(*tert*-Butyl)-5-methyl-2-phenyl-1H-benzo[d]imidazole (3i): White solid; Yield: 87% (22.9 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.5 Hz, 1H), 7.56 (s, 1H), 7.47 (d, *J* = 6.7 Hz, 2H), 7.45 – 7.39 (m, 3H), 7.10 (d, *J* = 8.5 Hz, 1H), 2.48 (s, 3H), 1.60 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.5, 143.6, 135.9, 132.9, 131.5, 129.7, 128.9, 127.7, 123.4, 119.8, 114.1, 58.7, 31.4, 21.2. HRMS (ESI-TOF) m/z: calculated for $C_{18}H_{20}N_2Na^+$: 287.1519 (M + Na)$^+$, found: 287.1529.

1-(*tert*-Butyl)-4,6-dimethyl-2-phenyl-1H-benzo[d]imidazole (3j): White solid; Yield: 91% (25.3 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, *J* = 6.7 Hz, 2H), 7.45 – 7.38 (m, 3H), 7.35 (s, 1H), 6.93 (s, 1H), 2.64 (s, 3H), 2.50 (s, 3H), 1.59 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.2, 140.6, 136.2, 134.7, 131.4, 129.9, 129.3, 128.8, 127.7, 123.8, 112.2, 58.6, 31.4, 22.1, 16.9. HRMS (ESI-TOF) m/z: calculated for $C_{19}H_{22}N_2Na^+$: 301.1675 (M + Na)$^+$, found: 301.1680.

1-(*tert*-Butyl)-2-(p-tolyl)-1H-benzo[d]imidazole (3k): White solid; Yield: 94% (24.8 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 8.5, 4.3 Hz, 1H), 7.71 (dd, *J* = 8.5, 4.3 Hz, 1H), 7.36 (d, *J* = 7.9 Hz, 2H), 7.28 – 7.25 (m, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 2.42 (s, 3H), 1.62 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.8, 143.3, 138.8, 134.9, 132.8, 129.5, 128.4, 121.8, 121.7, 120.1, 114.6, 58.8, 31.4, 21.4. HRMS (ESI-TOF) m/z: calculated for $C_{18}H_{20}N_2Na^+$: 287.1519 (M + Na)$^+$, found: 287.1521.

1-(*tert*-Butyl)-2-(4-methoxyphenyl)-1H-benzo[d]imidazole (3l): White solid; Yield: 83% (23.2 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 – 7.74 (m, 1H), 7.74 – 7.69 (m, 1H), 7.39 (d, *J* = 8.6 Hz, 2H), 7.28 – 7.25 (m, 2H), 6.94 (d, *J* = 8.6 Hz, 2H), 3.86 (s, 3H), 1.62 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.1, 153.5, 143.2, 134.9, 130.9, 127.9, 121.8, 121.7, 120.1, 114.6, 113.2, 58.9, 55.3, 31.4. HRMS (ESI-TOF) m/z: calculated for $C_{18}H_{20}N_2NaO^+$:303.1468 (M + Na)$^+$, found: 303.1472.

2-([1,1'-Biphenyl]-4-yl)-1-(*tert*-butyl)-1H-benzo[d]imidazole (3m): White solid; Yield: 95% (30.9 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 – 7.78 (m, 1H), 7.77 – 7.72 (m, 1H), 7.66 (dd, *J* = 8.0, 1.7 Hz, 4H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.31 – 7.27 (m, 2H), 1.67 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.3, 143.3, 141.7, 140.3, 135.0, 134.7, 130.1, 128.8, 127.6, 127.1, 126.4, 122.0, 121.8, 120.2, 114.7, 58.9, 31.5. HRMS (ESI-TOF) m/z: calculated for $C_{23}H_{22}N_2Na^+$: 349.1675 (M + Na)$^+$, found: 349.1676.

1-(*tert*-Butyl)-2-(4-fluorophenyl)-1H-benzo[d]imidazole (3n): White solid; Yield: 82% (22.1 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 – 7.75 (m, 1H), 7.75 – 7.70 (m, 1H), 7.46 (dd, *J* = 8.5, 5.4 Hz, 2H), 7.30 – 7.27 (m, 2H), 7.12 (t, *J* = 8.6 Hz, 2H), 1.62 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.1 (d, *J* = 248.7 Hz), 152.4, 143.2, 134.9, 131.9 (d, *J* = 3.6 Hz), 131.5 (d, *J* = 8.5 Hz), 122.1, 122.0, 120.2, 114.9 (d, *J* = 22.1 Hz), 114.7, 59.0, 31.5. HRMS (ESI-TOF) m/z: calculated for $C_{17}H_{17}FN_2Na^+$: 291.1268 (M + Na)$^+$, found: 291.1279.

1-(*tert*-Butyl)-2-(4-chlorophenyl)-1H-benzo[d]imidazole (3o): White solid; Yield: 76% (21.7 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 6.1, 3.2 Hz, 1H), 7.72 (dd, *J* = 6.1, 3.2 Hz, 1H), 7.45 – 7.39 (m, 4H), 7.28 (dd, *J* = 6.1, 3.2 Hz, 2H), 1.62 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.2, 143.2, 135.2, 134.9, 134.3, 131.0, 128.1, 122.2, 122.0, 120.2, 114.7, 59.0, 31.5. HRMS (ESI-TOF) m/z: calculated for $C_{17}H_{17}ClN_2Na^+$: 307.0972 (M + Na)$^+$, found: 307.0985.

1-(*tert*-Butyl)-2-(4-(trifluoromethyl)phenyl)-1H-benzo[d]imidazole (3p): White solid; Yield: 89% (28.3

mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 6.3, 2.9 Hz, 1H), 7.74 (dd, *J* = 6.3, 2.9 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.33 – 7.28 (m, 2H), 1.63 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.8, 143.2, 139.6, 134.9, 131.2 (q, *J* = 34.2 Hz), 130.2, 124.8 (q, *J* = 3.8 Hz), 123.0, 122.5, 122.2, 120.3, 114.7, 59.1, 31.8. HRMS (ESI-TOF) m/z: calculated for $C_{18}H_{17}F_3N_2Na^+$: 341.1236 (M + Na)$^+$, found: 341.1242.

Methyl 4-(1-(*tert*-butyl)-1H-benzo[d]imidazol-2-yl)benzoate (3q): White solid; Yield: 93% (28.6 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.2 Hz, 2H), 7.81 – 7.76 (m, 1H), 7.76 – 7.71 (m, 1H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.31 – 7.27 (m, 2H), 3.96 (s, 3H), 1.62 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.6, 152.3, 143.3, 140.5, 134.9, 130.6, 129.8, 129.0, 122.3, 122.1, 120.3, 114.7, 59.0, 52.3, 31.5. HRMS (ESI-TOF) m/z: calculated for $C_{19}H_{20}N_2NaO_2^+$: 331.1417 (M + Na)$^+$, found: 331.1428.

4-(1-(*tert*-Butyl)-1H-benzo[d]imidazol-2-yl)benzonitrile (3r): Wite solid; Yield: 91% (25.0 mg,); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 – 7.76 (m, 1H), 7.74 (d, *J* = 8.3 Hz, 3H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.34 – 7.28 (m, 2H), 1.63 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.2, 143.3, 140.7, 134.9, 131.6, 130.5, 122.7, 122.3, 120.4, 118.3, 114.8, 113.0, 59.1, 31.6. HRMS (ESI-TOF) m/z: calculated for $C_{18}H_{17}N_3Na^+$: 298.1315 (M + Na)$^+$, found: 298.1322.

1-(*tert*-Butyl)-2-(m-tolyl)-1H-benzo[d]imidazole (3s): White solid; Yield: 96% (25.4 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 – 7.76 (m, 1H), 7.74 – 7.70 (m, 1H), 7.33 – 7.25 (m, 6H), 2.40 (s, 3H), 1.63 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.8, 143.3, 137.5, 135.7, 134.8, 130.2, 129.6, 127.5, 126.8, 121.8, 121.7, 120.1, 114.6, 58.8, 31.4, 21.3. HRMS (ESI-TOF) m/z: calculated for $C_{18}H_{20}N_2Na^+$: 287.1519 (M + Na)$^+$, found: 287.1511.

1-(*tert*-Butyl)-2-(3-methoxyphenyl)-1H-benzo[d]imidazole (3t): White solid; Yield: 81% (22.7 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 – 7.77 (m, 1H), 7.74 – 7.71 (m, 1H), 7.32 (t, *J* = 7.9 Hz, 1H), 7.29 – 7.25 (m, 2H), 7.06 (d, *J* = 7.5 Hz, 1H), 7.04 (s, 1H), 7.00 (dd, *J* = 8.3, 2.0 Hz, 1H), 3.84 (s, 3H), 1.64 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.9, 153.3, 143.2, 137.0, 134.8, 128.8, 122.4, 122.0, 121.8, 120.2, 115.1, 114.9, 114.6, 58.9, 55.3, 31.3. HRMS (ESI-TOF) m/z: calculated for $C_{18}H_{20}N_2NaO^+$:303.1468 (M + Na)$^+$, found: 303.1462.

1-(*tert*-Butyl)-2-(3-fluorophenyl)-1H-benzo[d]imidazole (3u): White solid; Yield: 94% (25.1 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 – 7.77 (m, 1H), 7.74 – 7.71 (m, 1H), 7.40 (dd, *J* = 13.8, 7.8 Hz, 1H), 7.32 – 7.27 (m, 3H), 7.22 (d, *J* = 8.9 Hz, 1H), 7.17 (td, *J* = 8.5, 1.9 Hz, 1H), 1.64 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.9 (d, *J* = 248.3 Hz), 151.9 (d, *J* = 2.4 Hz), 143.2, 137.8 (d, *J* = 8.1 Hz), 134.8, 129.4 (d, *J* = 8.3 Hz), 125.7 (d, *J* = 3.1 Hz), 122.3, 122.0, 120.3, 117.0 (d, *J* = 22.1 Hz), 116.1 (d, *J* = 20. 6 Hz), 114.7, 59.0, 31.4. HRMS (ESI-TOF) m/z: calculated for $C_{17}H_{17}FN_2Na^+$: 291.1268 (M + Na)$^+$, found: 291.1265.

1-(*tert*-Butyl)-2-(o-tolyl)-1H-benzo[d]imidazole (3v): White solid; Yield: 98% (25.8 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 – 7.77 (m, 1H), 7.76 – 7.71 (m, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.31 (d, *J* = 7.2 Hz, 1H), 7.30 – 7.27 (m, 2H), 7.25 – 7.21 (m, 2H), 2.18 (s, 3H), 1.59 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.5, 143.6, 137.2, 135.6, 134.4, 129.9, 129.7, 129.1, 125.1, 121.8, 121.6, 120.1, 114.5, 58.7, 30.7, 19.9. HRMS (ESI-TOF) m/z: calculated for $C_{18}H_{20}N_2Na^+$: 287.1519 (M + Na)$^+$, found: 287.1509.

1-(*tert*-Butyl)-2-(2-fluorophenyl)-1H-benzo[d]imidazole (3w): White solid; Yield: 93% (24.9 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 – 7.77 (m, 1H), 7.76 – 7.72 (m, 1H), 7.49 (td, *J* = 7.4, 1.4 Hz, 1H), 7.47 – 7.43 (m, 1H), 7.31 – 7.27 (m, 2H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 8.9 Hz, 1H), 1.65 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.4 (d, *J* = 247.1 Hz), 147.3, 143.6, 134.8, 131.5 (d, *J* = 2.4 Hz), 131.3 (d, *J* = 8.0 Hz), 124.2 (d, J = 16.2 Hz), 123.9 (d, *J* = 3.5 Hz), 122.2, 121.8, 120.3, 115.4 (d, *J* = 20.2 Hz), 114.6, 58.9, 30.5. HRMS (ESI-TOF) m/z: calculated for $C_{17}H_{17}FN_2Na^+$: 291.1268 (M + Na)$^+$, found: 291.1275.

1-(*tert*-Butyl)-2-(3,4-dimethylphenyl)-1H-benzo[d]imidazole (3x): White solid; Yield: 94% (26.1 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 – 7.74 (m, 1H), 7.73 – 7.69 (m, 1H), 7.28 – 7.23 (m, 3H), 7.17 (q, *J* = 8.6 Hz, 2H), 2.32 (s, 3H), 2.30 (s, 3H), 1.63 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.9, 143.2, 137.4, 136.0, 134.9, 133.1, 130.6, 128.8, 127.1, 121.74, 121.67, 120.1, 114.6, 58.8, 31.4, 19.69, 19.67. HRMS (ESI-TOF) m/z: calculated for $C_{19}H_{22}N_2Na^+$: 301.1675 (M + Na)$^+$, found: 301.1678.

1-(*tert*-Butyl)-2-(naphthalen-2-yl)-1H-benzo[d]imidazole (3y): White solid; Yield: 96% (28.8 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.92 - 7.87 (m, 3H), 7.84 – 7.80 (m, 1H), 7.78 – 7.74 (m, 1H), 7.59 – 7.52 (m, 3H), 7.33 – 7.28 (m, 2H), 1.65 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.5, 143.4, 135.0, 133.2, 132.5, 129.1, 128.2, 127.8, 127.3, 127.2, 126.8, 126.6, 122.0, 121.9, 120.2, 114.7, 58.9, 31.5. HRMS (ESI-TOF) m/z: calculated for $C_{21}H_{20}N_2Na^+$: 323.1519 (M + Na)$^+$, found: 323.1528.

1-(*tert*-Butyl)-2-(furan-2-yl)-1H-benzo[d]imidazole (3z): White solid; Yield: 94% (22.6 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 – 7.78 (m, 1H), 7.77 – 7.71 (m, 1H), 7.55 (s, 1H), 7.30 – 7.27 (m, 2H), 6.76 (d, *J* = 3.1 Hz, 1H), 6.55 – 6.53 (m, 1H), 1.68 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.0, 143.6, 143.0, 142.5, 135.1, 122.8, 122.0, 120.7, 114.6, 112.6, 111.4, 59.2, 30.2. HRMS (ESI-TOF) m/z: calculated for $C_{15}H_{16}N_2NaO^+$: 263.1155 (M + Na)$^+$, found: 263.1159.

1-(*tert*-Butyl)-2-(thiophen-2-yl)-1H-benzo[d]imidazole (3aa): White solid; Yield: 93% (23.8 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 – 7.76 (m, 1H), 7.76 – 7.70 (m, 1H), 7.47 (dd, *J* = 5.1, 0.9 Hz, 1H), 7.29 – 7.27 (m, 2H), 7.25 (dd, *J* = 3.5, 0.9 Hz, 1H), 7.08 (dd, *J* = 5.1, 3.5 Hz, 1H), 1.70 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.5, 143.1, 135.2, 135.1, 130.3, 127.3, 126.3, 122.4, 122.0, 120.4, 114.7, 59.4, 31.0. HRMS (ESI-TOF) m/z: calculated for $C_{15}H_{16}N_2NaS^+$: 279.0926 (M + Na)$^+$, found: 279.0936.

1-(*tert*-Butyl)-2-(pyridin-4-yl)-1H-benzo[d]imidazole (3ab): White solid; Yield: 71% (17.8 mg); ^{1}H NMR (600

MHz, $CDCl_3$) δ 8.71 (d, *J* = 4.2 Hz, 2H), 7.78 (dd, *J* = 5.3, 3.9 Hz, 1H), 7.74 (dd, *J* = 5.3, 3.9 Hz, 1H), 7.45 (d, *J* = 5.7 Hz, 2H), 7.34 – 7.28 (m, 2H), 1.65 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.5, 149.3, 144.2, 143.3, 134.9, 124.5, 122.6, 122.3, 120.4, 114.8, 59.1, 31.5. HRMS (ESI-TOF) m/z: calculated for $C_{16}H_{17}N_3Na^+$: 274.1315 $(M + Na)^+$, found: 274.1314.

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References

[1] M. Smist, H. Kwiecien, *Curr. Org. Synth.* **2014**, *11*, 676.

[2] a) M. Alamgir, D. S. C. Black, N. Kumar, in: *Bioactive Heterocycles III* (Eds.: M.T.H. Khan), Springer, Berlin, **2007**, pp. 87-118; b) B. V. S. Kumar, S. D. Vaidya, R. V. Kumar, S. B. Bhirud, R. B. Mane, *Eur. J. Med. Chem.* **2006**, *41*, 599; c) K. M. Hosamani, H. M. Seetharamareddy, R. S. Keri, M. S. Hanamanthagouda, M. G. Moloney, *J. Enzy. Inhibi. Med. Chem.* **2009**, *24*, 1095; d) T. D. Penning, G. D. Zhu, V. B. Gandhi, J. Gong, X. Liu, Y. Shi, V. Klinghofer, E. F. Johnson, C. K. Donawho, D. J. Frost, V. B. Diaz, J. J. Bouska, D. J. Osterling, A. M. Olson, K. C. Marsh, V. L. Giranda, *J. Med. Chem.* **2009**, *52*, 514; e) H. M. Refaat, *Eur. J. Med. Chem.* **2010**, *45*, 2949.

[3] G. Yadav, S. Ganguly, *Eur. J. Med. Chem.* **2015**, *97*, 419.

[4] a) H. M. Smith, *High Performance Pigments*, Wiley−VCH, Weinheim, **2002**, pp. 135−158; b) B. Meuthen, A. S. Jandel, *Coil Coating II*, Vieweg & Sohn, Wiesbaden, **2008**, pp. 65; c) G. G. Scherer, *Fuel Cells II*, Springer, Berlin, **2008**, pp. 65−120; d) J. A Asensio, P. Gomez-Romero, *Fuel Cells.* **2005**, *5*, 336; e) A. Sannigrahi, D. Arunbabu, R. M. Sankar, T. Jana, *Macromolecules*, **2007**, *40*, 2844; f) M. J. Plater, P. Barnes, L. K. McDonald, S. Wallace, N. Archer, T. Gelbrich, P. N. Horton, M. B. Hursthouse, *Org. Biomol. Chem.* **2009**, *7*, 1633.

[5] a) X. -X. Guo, D. -W. Gu, Z. Wu, W. Zhang, *Chem. Rev.*, **2015**, *115*, 1622; b) L. C. R. Carvalho, E. Fernandes, N. M. B. Marques, *Chem. Eur. J.* **2011**, *17*, 12544.

[6] a) E. C. Wagner, W. H. Millett, *Org. Synth.*, **1939**, *19*, 12; b) Y.-X. Chen, L.-F. Qian, W. Zhang, B. Han, *Angew. Chem. Int. Ed.* **2008**, *47*, 9330; c) C. Zhang, L. Zhang, N. Jiao, *Green Chem.* **2012**, *14*, 3273; d) T. B. Nguyen, L. Ermolenko, W. A. Dean, A. Mourabit, *Org. Lett.* **2012**, *4*, 5948; e) G. Bastug, C. Eviolitte, I. E. Markó, *Org. Lett.* **2012**, *14*, 3502; f) P. Daw, Y. Ben-David, D. Milstein, *ACS Catal.* **2017**, *7*, 7456; g) L. Li, Q. Luo, H. Cui, R. Li, J. Zhang, T. Peng, *ChemCatChem.* **2018**, *10*, 1607.

[7] a) B. Zou, Q. Yuan, D. Ma, *Angew. Chem. Int. Ed.* **2007**, *46*, 2598; b) N. Zheng, K. W. Anderson, X. Huang, H. N. Nguyen, S. L. Buchwald, *Angew. Chem. Int. Ed.* **2007**, *46*, 7509; c) G. Brasche, S. L. Buchwald, *Angew. Chem. Int. Ed.* **2008**, *47*, 1932; d) Q. Xiao, W.-H. Wang, G. Liu, F.-K. Meng, J.-H. Chen, Z. Yang, Z.-J. Shi, *Chem. Eur. J.* **2009**, *15*, 7292; e) J. Li, S. Béenard, L. Neuville, J. Zhu, *Org. Lett.* **2012**, *14*, 5980; f) H. Baars, S. Beyer, S. V. Kohlhepp, C. Bolm, *Org. Lett.* **2014**, *16*, 536; g) J. Xia, X. Yang, Y. Li, X. Li, *Org. Lett.* **2017**, *19*, 3243; h) T. Liang, Z. Tan, H. Zhao, X. Chen, H. Jiang, M. Zhang, *ACS Catal.* **2018**, *8*, 2242. i) C. T. Brain, J. T. Steer, *J. Org. Chem.* **2003**, *68*, 6814; j) P. Saha, T. Ramana, N. Purkait, M. A. Ali, R. Paul, T. Punniyamurthy, *J. Org. Chem.* **2009**, *74*, 8719; k) M. M. Guru, M. A. Ali, T. Punniyamurthy, *J. Org. Chem.* **2011**, *76*, 5295; l) P. S, M. A. Ali, P. Ghosh, T. Punniyamurthy, *Org. Biomol. Chem.* **2010**, *8*, 5692; m) S. K. Alla, R. K. Kumar, P. Sadhu, T. Punniyamurthy, *Org. Lett.* **2013**, *15*, 1334; n) C. T. Brain, S. A. Brunton, *Tetrahedron Lett.* **2002**, *43*,1893.

[8] a) C. Juan, P. Pilar, C. Ernesto, *Coordin. Chem. Rev.* **1999**, *193*, 207; b) A. Steffen, R. M. Ward, W. D. Jones, T. B. Marder, *Coordin. Chem. Rev.* **2010**, *254*, 1950.

[9] a) G. Dyker, *Angew. Chem. Int. Ed.* **1992**, *31*, 1023; b) G. Dyker, *Angew. Chem. Int. Ed.* **1994**, *33*, 103; c) M. A. Campo, R. C. Larock, *J. Am. Chem. Soc.* **2002**, *124*, 14326; d) G. Karig, M.-T. Moon, N. Thasana, T. Gallagher, *Org. Lett.* **2002**, *4*, 3115; e) D. Masselot, J. P. H. Charmant, T. Gallagher, *J. Am. Chem. Soc.* **2006**, *128*, 694; f) T. Piou, A. Bunescu, Q. Wang, L. Neuville, J. Zhu, *Angew. Chem. Int. Ed.* **2013**, *52*, 12385; g) R. Deng, Y. Huang, X. Ma, G. Li, R. Zhu, B. Wang, Y.-B. Kang, Z. Gu, *J. Am. Chem. Soc.* **2014**, *136*, 4472; h) D.-W. Gao, Q. Yin, Q. Gu, S.-L. You, *J. Am. Chem. Soc.* **2014**, *136*, 4841; i) M. Sickert, H. Weinstabl, B. Peters, X. Hou, M. Lautens, *Angew. Chem. Int. Ed.* **2014**, *53*, 5147; j) M. Wang, X. Zhang, Y.-X. Zhuang, Y.-H. Xu, T.-P. Loh, *J. Am. Chem. Soc.* **2015**, *137*, 1341; k) J. Ye, Z. Shi, T. Sperger, Y. Yasukawa, C. Kingston, F. Schoenebeck, M. Lautens, *Nat. Chem.* **2016**, *9*, 361; l) T.-J. Hu, G. Zhang, Y.-H. Chen, C.-G. Feng, G.-Q. Lin, *J. Am. Chem. Soc.* **2016**, *138*, 2897; m) Á. Gutiérrez-Bonet, F. Juliá-Hernández, B. de Luis, R. Martin, *J. Am. Chem. Soc.* **2016**, *138*, 6384; n) M. Pérez-Gómez, J.-A. García-López, *Angew. Chem. Int. Ed.* **2016**, *55*, 14389; o) H. Yoon, A. Lossouarn, F. Landau, M. Lautens, *Org. Lett.* **2016**, *18*, 6324; p) D. Chen, G. Shi, H. Jiang, Y. Zhang, Y. Zhang, *Org. Lett.* **2016**, *18*, 2130; q) L. Yang, R. Melot, M. Neuburger, O. Baudoin, *Chem. Sci.* **2017**, *8*, 1344; r) T. Yao, D. He, *Org. Lett.* **2017**, *19*, 842; s) M. M. Pérez-Gómez, S. Hernández-Ponte, D. Bautistab, J.-A. García-López, *Chem. Commun.* **2017**, *53*, 2842; t) A. Lu, X. Ji, B. Zhou, Z. Wu, Y. Zhang, *Angew. Chem. Int. Ed.* **2018**, *57*, 3233.

[10] a) H. Jiang, Y. Zhang, D. Chen, B. Zhou, Y. Zhang, *Org. Lett.* **2016**, *18*, 2032; b) G. Shi, D. Chen, H. Jiang, Y. Zhang, Y. Zhang, *Org. Lett.* **2016**, *18*, 2958; c) S. Pan, H. Jiang, Y. Zhang, D. Chen, Y. Zhang, *Org. Lett.* **2016**, *18*, 5192; d) Z. Wu, D. Ma, B. Zhou,

10.1002/adsc.201801367

X. Ji, X. Ma, X. Wang, Y. Zhang, *Angew. Chem. Int. Ed.* **2017**, *56*, 12288; e) C. Shao, Z. Wu, X. Ji, B. Zhou, Y. Zhang, *Chem. Commun.***2017**, *53*, 10429; f) D. Ma, G. Shi, Z. Wu, X. Ji, Y. Zhang, *J. Org. Chem.* **2018**, *83*, 1065.

[11] a) J. Zhao, D. Yue, M. A. Campo, R. C. Larock, *J. Am. Chem. Soc.* **2007**, *129*, 5288. Several Pd-catalyzed reactions of 2-iodobenzimines with alkynes have been reported. However, the *C,C*-palladacycles were not invovled in the reactions as suggested: b) K. R. Roesch, R. C. Larock, *Org. Lett.* **1999**, *1*, 1551; c) K. R. Roesch, R. C. Larock, *J. Org. Chem.* **2001**, *66*, 412; d) W. Zhang, J. M. Ready, *Angew. Chem. Int. Ed.* **2014**, *53*, 8980.

[12] a) T. A. Ramirez, Q. Wang, Y. Zhu, H. Zheng, X. Peng, R. G. Cornwall, Y. Shi, *Org. Lett.* **2013**, *15*, 4210; b) H. Zheng, Y. Zhu, Y. Shi, *Angew. Chem. Int. Ed.* **2014**, *53*, 11280; c) C. Shao, B. Zhou, Z. Wu, X. Ji, Y. Zhang, *Adv. Synth. Catal.* **2018**, *360*, 887; d) B. Zhou, Z. Wu, D. Ma, X. Ji, Y. Zhang, *Org. Lett*. **2018**, *20*, 6440.

[13] a) K. Ouyang, Z. Xi, *Acta Chim. Sinica* **2013**, *71*, 13; b) C. Amatore, A. Jutand, *Acc. Chem. Res.* **2000**, *33*, 314; c) M. Lafrance, C. N. Rowley, T. K. Woo, K. Fagnou, *J. Am. Chem. Soc.* **2006**, *128*, 8754; d) J. C. Gaunt, B. L. Shaw, *J. Organomet. Chem.* **1975**, *102*, 511.

[14] K. L. Kirk, *J. Org. Chem.* **1978**, *43*, 4381.

[15] a) C. Chen, G. Shang, J. Zhou, Y. Yu, B. Li, J. Peng, *Org. Lett.* **2014**, *16*, 1872; b) S. J. A. Varela, C. Saá, *Org. Lett.* **2017**, *19*, 1702; c) J. Peng, G. Shang, C. Chen, Z. Miao, B. Li, *J. Org. Chem.* **2013**, *78*, 1242;

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