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# Suzuki–Miyaura cross-coupling of bulky anthracenyl carboxylates by using pincer nickel N-heterocyclic carbene complexes: an efficient protocol to access fluorescent anthracene derivatives†

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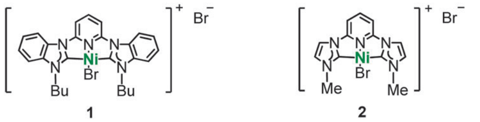
**A series of fluorescent (hetero)-aryl substituted anthracene derivatives were readily accessible from the corresponding bulky anthracen-9-yl carboxylates *via* Suzuki–Miyaura cross-coupling reactions by using pincer nickel N-heterocyclic carbene complex 1 even at the catalyst loading as low as 0.1 mol% in the presence of catalytic amounts of PCy$_3$.**

Since the first observation of organic electroluminescence from anthracene crystals in the 1960s, (hetero)-aryl substituted anthracene compounds have attracted considerable attention and constituted fascinating building blocks to fabricate various optoelectronic devices in organic light-emitting diodes (OLEDs).[1] Therefore, a great number of synthetic protocols have been developed,[2–5] most of which focused on simple functionalization of the anthracene core. Besides the addition of Grignard or lithium reagents to anthraquinone,[4] Suzuki–Miyaura cross-coupling of halogenated anthracenes constituted a preferred protocol.[1,5,6]

Besides aryl halides, recently, phenolic sulfonates and sulfamates have been successfully applied as electrophiles in the Suzuki–Miyaura cross-coupling reactions.[6,7] Moreover, less studied aryl carboxylates represent inactive electrophiles with better stability and less toxicity for cross-coupling reactions. The essential obstacle for applicability of aryl carboxylates is the difficulty in achieving selective activation of inert C$_{aryl}$–O bonds rather than C$_{carbonyl}$–O bonds.[8] Until very recently, Shi and Garg groups realized the first examples of the cross-coupling between aryl pivalates and aryl boronic reagents by using nickel catalysts containing air-sensitive phosphine ligands,[9] which could be further extended to other carboxylates and carbamates.[7,10] Besides these achievements, the applicability of the protocol is still hindered by: (1) high catalyst loadings (usually 20 mol% is required); (2) tedious handling steps required for air-sensitive catalysts; and (3) sterically hindered substrates, which remains a challenging task. Especially, the study on the coupling with bulky anthracenyl carboxylates is neglected.

As strong σ-donors and weak π-acceptors, robust N-heterocyclic carbenes (NHCs) have been regarded as suitable replacements for the traditional air-sensitive phosphine ligands.[11] The catalysts derived from NHCs may also be applicable to the selective C–O activation in the coupling of aryl carboxylates. However, the examples of Ni–NHC catalyzed cross-coupling reactions with inactive aryl carboxylates are still rare, in which air-sensitive Ni(COD)$_2$ has to be involved.[10b,e] Recently, our group found that robust pyridine-bridged bis-benzimidazolylidene pincer nickel complex **1** not only efficiently catalyzes the Suzuki–Miyaura cross-coupling reactions with various aryl halides, but also well tolerates electron-rich, sterically demanding and heterocyclic inert aryl tosylates and mesylates with a catalytic amount of PPh$_3$ as a reductant (Scheme 1).[12f] Following our recent research interest in the synthesis of metal complexes and their potential applications in catalysis and soft materials,[12–14] we would like to explore the applicability of robust complex **1** in Suzuki–Miyaura cross-coupling reactions with challenging sterically bulky anthracenyl carboxylates and further study the fluorescence properties of the resulting (hetero)-aryl substituted anthracene derivatives.

Initially, the reaction between phenyl-boronic acid and anthracen-9-yl pivalate **3** was selected to optimize the reaction conditions (Table 1). According to our previous results,[12f] a catalytic amount of PPh$_3$ was applied as a reductant. However, in the presence of 2 mol% complex **1** and 4.5 equiv. of K$_3$PO$_4$·H$_2$O, an unsatisfactory result was observed in 1.5 mL toluene at 100 °C for 24 hours with 8 mol% PPh$_3$ (4%, Table 1, entry 1). When PCy$_3$ was applied instead, pivalate **3** was completely converted to



**Scheme 1** Pyridine-bridged pincer NHC nickel complexes **1** and **2**.

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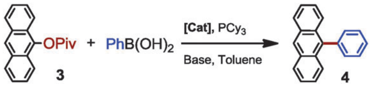
**Table 1** Optimization of the reaction conditions[a]



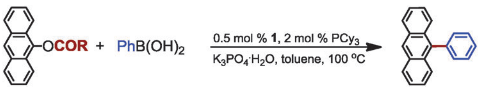
| Entry | [Cat] | Base | Yield[b] (%) |
|---|---|---|---|
| 1 | **1** (2 mol%) | $K_3PO_4 \cdot H_2O$ | 4[c] |
| 2 | **1** (2 mol%) | $K_3PO_4 \cdot H_2O$ | 97 |
| 3 | **1** (1 mol%) | $K_3PO_4 \cdot H_2O$ | 96 |
| 4 | **1** (0.5 mol%) | $K_3PO_4 \cdot H_2O$ | 96 |
| 5 | **1** (0.5 mol%) | $K_3PO_4 \cdot 3H_2O$ | 93 |
| 6 | **1** (0.5 mol%) | $K_3PO_4$ | 79 |
| 7 | **1** (0.5 mol%) | KOH | 93 |
| 8 | **1** (0.5 mol%) | $K_3PO_4 \cdot H_2O$ | 97[d] |
| 9 | **1** (0.5 mol%) | $K_3PO_4 \cdot H_2O$ | 27[d,e] |
| 10 | **1** (0.1 mol%) | $K_3PO_4 \cdot H_2O$ | 82[d] |
| 11 | **1** (0.5 mol%) | $K_3PO_4 \cdot H_2O$ | 18[d,f] |
| 12 | — | $K_3PO_4 \cdot H_2O$ | n.r.[d] |
| 13 | $NiBr_2$ (0.5 mol%) | $K_3PO_4 \cdot H_2O$ | n.r.[d] |
| 14 | $NiCl_2(PCy_3)_2$ (0.5 mol%) | $K_3PO_4$ | 93[d,g] |
| 15 | **2** (0.5 mol%) | $K_3PO_4 \cdot H_2O$ | 83[d] |

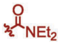
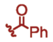
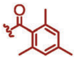
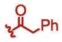
[a] In a 0.5 mmol scale with $PCy_3$ in 1.5 mL toluene at 100 °C for 6 h. [b] Isolated yield. [c] With $PPh_3$ for 24 h. [d] In 3 mL toluene. [e] At 80 °C. [f] Without $PCy_3$. [g] For 24 h.

product **4** and resulted in a nearly quantitative yield (97%, Table 1, entry 2). When the catalyst was reduced to 0.5 mol%, no obvious decrease of the yield was found (Table 1, entries 3 and 4). The trace amount of water played a crucial role in the coupling process: $K_3PO_4 \cdot 3H_2O$ resulted in a slightly lower yield, whereas, anhydrous $K_3PO_4$ led to an inferior yield (96% *vs.* 93% and 79%; Table 1, entry 4 *vs.* 5 and 6). To our surprise, a good yield was still obtained when KOH was selected as a base,[15] and only a small amount of anthrone hydrolyzed from esters was detected (Table 1, entry 7). Other inorganic and organic bases all resulted in unsatisfactory yields (ESI†). After screening various solvents, toluene was still the best choice (ESI†). A slightly higher yield was observed in the diluted case (3 mL, 97%, Table 1, entry 8). Lower temperature led to a worse result (27%, Table 1, entry 9). Under the optimal conditions, even with 0.1 mol% **1** and 0.4 mol% $PCy_3$, an 82% isolated yield was still obtained (Table 1, entry 10). A very poor yield was observed without $PCy_3$, and even no reaction occurred in the absence of pincer complex **1** (Table 1, entries 11 and 12). When $NiBr_2$ was utilized instead, no product was detected by GC-MS (Table 1, entry 13). All these results indicate that NHC ligands improve the catalytic activation of the nickel center. The known catalytic system ($NiCl_2(PCy_3)_2$, $K_3PO_4$, toluene)[9b] developed by Grag led to a slightly inferior yield, and **3** is hardly converted even after 24 h (93%, Table 1, entry 14). Other reductants such as Zn and phenylboronic acid pinacol ester revealed much poor results (ESI†). Moreover, in comparison with complex **1**, its imidazolium analogue **2** only resulted in a moderate yield (83%, Table 1, entry 15), which confirmed that the extended aromatic rings of the NHC ligand lead to higher catalytic efficiency.[12,13]

With these exciting results in hand, the role of the carboxylate part was examined with a variety of esters (Table 2). The carbamate analogue was also proved to be an effective substrate under optimal reaction conditions, and an almost quantitative yield was observed (>99%, Table 1, entry 2). In contrast to the coupling of anthracen-9-yl pivalate, slightly inferior yields were obtained when other aliphatic carboxylates such as the isobutyrate, propionate, and acetate analogues, as well as benzoate, were employed (97% *vs.* 71–89%, Table 2, entry 1 *vs.* 3–6). Bulkier 2,4,6-trimethylbenzoate resulted in a better yield with an increased catalyst loading (95%, Table 2, entry 7). However, even with 5 mol% catalyst, anthracen-9-yl phenylacetate only resulted in a 19% yield along with a large amount of hydrolyzed anthrone, which may suggest that selective activation of $C_{aryl}$–O bonds in the sterically hindered carboxylates was favourable.

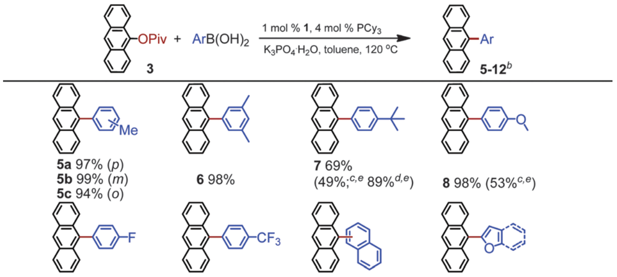
**Table 2** Suzuki–Miyaura cross-coupling reactions of phenylboronic acids with different esters derived from anthrone[a]



| Entry | –COR | Yield[b] (%) | Entry | –COR | Yield[b] (%) |
|---|---|---|---|---|---|
| 1 |  | 97 | 5 |  | 75 |
| 2 |  | >99 | 6 |  | 89 |
| 3 |  | 71 | 7 |  | 31 (95[c]) |
| 4 |  | 86 | 8 |  | 19[c] |

[a] The reactions were carried out in a 0.5 mmol scale at 100 °C for 6 h. [b] Isolated yield. [c] With 5 mol% complex **1** and 20 mol% $PCy_3$ for 24 h.

From Table 2, sterically hindered pivalates and carbamate are found to be most reactive. Therefore, the substrate scope of various (hetero)-arylboronic acids with pivalate **3** was then explored and the results are depicted in Scheme 2. However, in the presence of 0.5 mol% catalyst **1**, besides phenylboronic acid, pivalate **3** was hardly converted to products when other (hetero)-arylboronic acids were involved. Only moderate yields were obtained when 4-*tert*-butyl and 4-methoxy phenyl substituted boronic acids were applied. To our delight, when the catalyst loading was slightly increased to 1 mol%, full conversion was achieved in most cases at 120 °C with extended reaction time. In the case of arylboronic acids with electron-donating groups, up to quantitative isolated yields were obtained (**5**–**8**, Scheme 2). The relative position of substituents hardly has an impact on the coupling efficiency; similar isolated yields were observed with *p*, *m*, and *o*-tolylboronic acids



[a] 0.5 mmol scale at 120 °C for 12 h. [b] Isolated yield. [c] With 0.5 mol% catalyst. [d] With 2 mol% catalyst. [e] For 24 h.

**Scheme 2** Suzuki–Miyaura cross-coupling reactions of **3** with various aryl boronic acids[a].

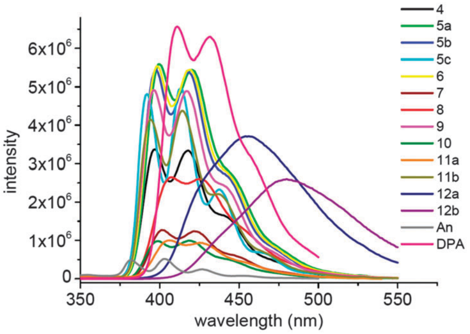


**Fig. 1** The fluorescence spectra of compounds **4–12**, An and DPA, measured in $CH_2Cl_2$ ($2 \times 10^{-5}$ mol $L^{-1}$) at room temperature, excitation wavelength at 263 nm.

(**5a–c**, 94–99%, Scheme 2). The protocol is also suitable for 3,5-dimethylphenyl-, 4-*tert*-butylphenyl and 4-methoxyphenylboronic acids (**6–8**, 89–98%, Scheme 2); in some cases, the reaction time had to be extended to 24 h to achieve satisfactory yields. However, when more sterically hindered 2,6-dimethylphenylboronic acid was applied, no product was detected and most of **3** was recovered. Delightedly, the arylboronic acids containing fluoridated electron-withdrawing groups were also well tolerated when 2 mol% complex **1** was applied (**9** and **10**, Scheme 2). In the case of substituted groups with coordination ability, such as 4-cyano- and 4-formylphenylboronic acids, no products were observed. Furthermore, 2-naphthylboronic acid resulted in an almost quantitative yield, whereas the 1-naphthyl analogue only revealed a moderate outcome (>99% *vs.* 46%, **11a** *vs.* **11b**, Scheme 2). Finally, the heteroarylboronic acids were also involved in the substrate scope test. Furan-2-boronic acid resulted in a moderate yield (**12a**, 56%, Scheme 2), whereas only a 16% yield of **12b** was obtained when benzo[*b*]furan-2-boronic acid was applied in the reaction (Scheme 2). A poor yield was observed in the case of 1-methyl-1*H*-indol-5-yl boronic acid (7%, ESI†). As expected, no corresponding products formed for other heteroarylboronic acids with strong coordination ability, such as (benzo)thiophen-2-yl or 4-pyridinyl boronic acid.

With a series of (hetero)-aryl substituted anthracene derivatives in hand, the study on their fluorescence properties in solution was carried out. Fig. 1 shows the fluorescence spectra of the anthracene derivatives **4–12** along with the well-known fluorescent compounds anthracene (An) and 9,10-diphenylanthracene (DPA). Upon excitation at 263 nm, all 9-arylanthracenes (**4–11**) exhibited similar blue emissions of An and DPA ranging from 382 nm to 432 nm. In comparison with **4**, a relative red-shift was observed with anthracene derivatives **7**, **8** and **11a**, whereas a slight blue-shift was found with analogues **5c** and **11b**. The heterocyclic substitutions affected the emission: 2-furanyl and 2-benzofuranyl derivatives **12a,b** exhibited rather different emission peaks, which were obviously red-shifted.

In summary, a series of strong fluorescent (hetero)-aryl substituted anthracene derivatives were synthesized through Suzuki–Miyaura cross-coupling reactions between anthracen-9-yl pivalate and (hetero)-arylboronic acids *via* selective C–O bond activation. Pyridine-bridged bis-benzimidazolylidene pincer nickel complex **1** was proved to be an effective catalyst in this transformation with the catalyst loading as low as 0.1 mol%. Furthermore, our new developed protocol is also applicable to the coupling of other challenging inactive anthracenyl carboxylates. All these results indicate that NHCs are also suitable ligands in the selective C–O bond activation coupling reactions.

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