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Accelerated Zincations for an Efficient and Mild Functionalization of Aromatics and Heterocycles

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Abstract: An improved process for the preparation of aromatic and heteroaromatic diorganozinc reagents and their subsequent reaction with electrophiles is presented. The new method, featuring the use of a 2,2,6,6-tetramethylpiperidyl (TMP) magnesium base in the presence of zinc chloride ($ZnCl_2$), is superior to the previous methods, which require the preparation of zinc bases. Specifically, the shorter reaction times under mild conditions provide an easier and more practical process, while the use of only a slight excess of the amide allows the isolation of products in high yields. These improvements are particularly significant for the large-scale preparation of organozincs and their subsequent reactions. Remarkably, beside the high kinetic activity, a wide range of functional groups is tolerated and sensitive heteroaromatics can easily be converted into the corresponding organometallic reagents and reacted with various electrophiles.

Keywords: cross-coupling; Grignard reaction; heterocycles; metalation; synthetic methods; zinc

The directed *ortho*-metalation of aromatic and heterocyclic compounds is an efficient method for the functionalization of these scaffolds.[1] Besides conventional lithium bases a range of new bimetallic ate-bases has been introduced by Kondo, Mulvey, Mongin and Uchiyama.[2] These bases allow a smooth metalation of a number of unsaturated systems due to synergetic effects between the two metals. Recently, we have also reported highly soluble metal amides complexed by LiCl such as TMPMgCl·LiCl (**1**),[3] (TMP = 2,2,6,6-tetramethylpiperidyl), $TMP_2Mg\cdot2LiCl$ (**2**),[4] TMPZnCl·LiCl (**3**),[5] $TMP_2Zn\cdot2MgCl_2\cdot2LiCl$ (**4**)[6] and $TMP_3Al\cdot3LiCl$[7] which allowed a chemo- and regioselective metalation of a broad range of functionalized aromatics and heteroaromatics. We have described an additional procedure involving a complexation of some organic substrates with $ZnCl_2$ prior to the addition of $TMP_2Mg\cdot2LiCl$ (**2**) which led to improved metalation yields.[8] However, this last method had several drawbacks: (i) the stability of $TMP_2Mg\cdot2LiCl$ (**2**) is limited due to its high kinetic basicity;[9] (ii) the tolerance of functional groups and sensitive heterocycles is also moderate.

Since we noticed that zincations may be performed at elevated temperatures,[10] we have envisioned to use the transmetalation energy to perform fast and efficient zincations at moderately elevated temperatures (reaction temperature up to 40 °C). Herein, we wish to report that this moderate increase of temperature leads to a dramatic decrease in the reaction time. Remarkably, this small temperature increase (10–15 °C) is sufficient to provide a rate acceleration of up to 50 times.

Thus, whereas the zincation of coumarin (**5**) with $TMP_2Zn\cdot2MgCl_2\cdot2LiCl$ (**4**) requires 4 h at 25 °C to reach >95% conversion, the sequential treatment of **5** with $ZnCl_2$ (0.5 equiv.) followed by the addition of TMPMgCl·LiCl (**1**; 1.1 equiv.) leads to the zincated species **6** within 2 h. If $ZnCl_2\cdot LiCl$[11] (0.5 equiv.) is used followed by the addition of TMPMgCl·LiCl (**1**; 1.1 equiv.) **6** is obtained *in 5 min* (Figure 1, Scheme 1).

After a Pd-catalyzed Negishi cross-coupling[12] with 4-iodoanisole, the expected coumarin derivative **7** is obtained in 82% yield (Scheme 1). A similar behaviour is found for quinoxaline (**8**). The addition of $TMP_2Zn\cdot2MgCl_2\cdot2LiCl$ (**4**, 0.55 equiv.) provides the diheteroaryl zinc reagent **9** after 5 h at 25 °C. Whereas the sequential treatment of the substrate with $ZnCl_2$ (0.5 equiv.) followed by the addition of TMPMgCl·LiCl (**1**; 1.1 equiv.) leads to the zincated species **9** in >95% within 2 h. In this case also the usage of $ZnCl_2\cdot LiCl$ (0.5 equiv.) followed by TMPMgCl·LiCl (**1**; 1.1 equiv.) accelerates the metalation and leads to complete conversion within 1 h. The

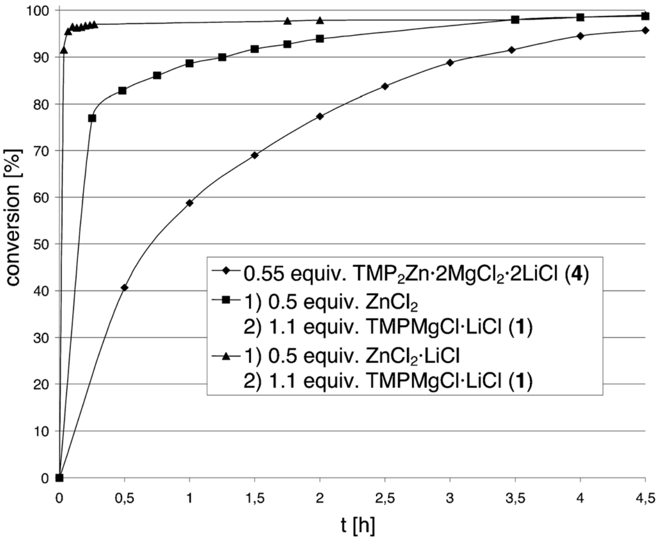


Figure 1. Progress of the metalation of coumarin (**5**) using different metalation procedures.

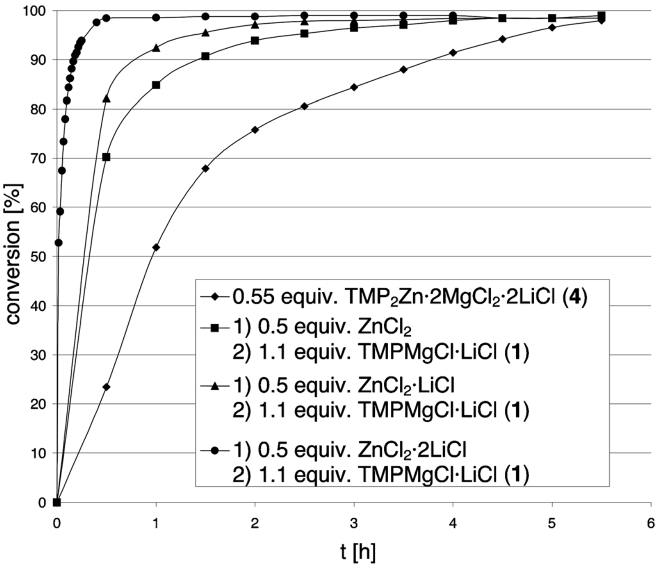
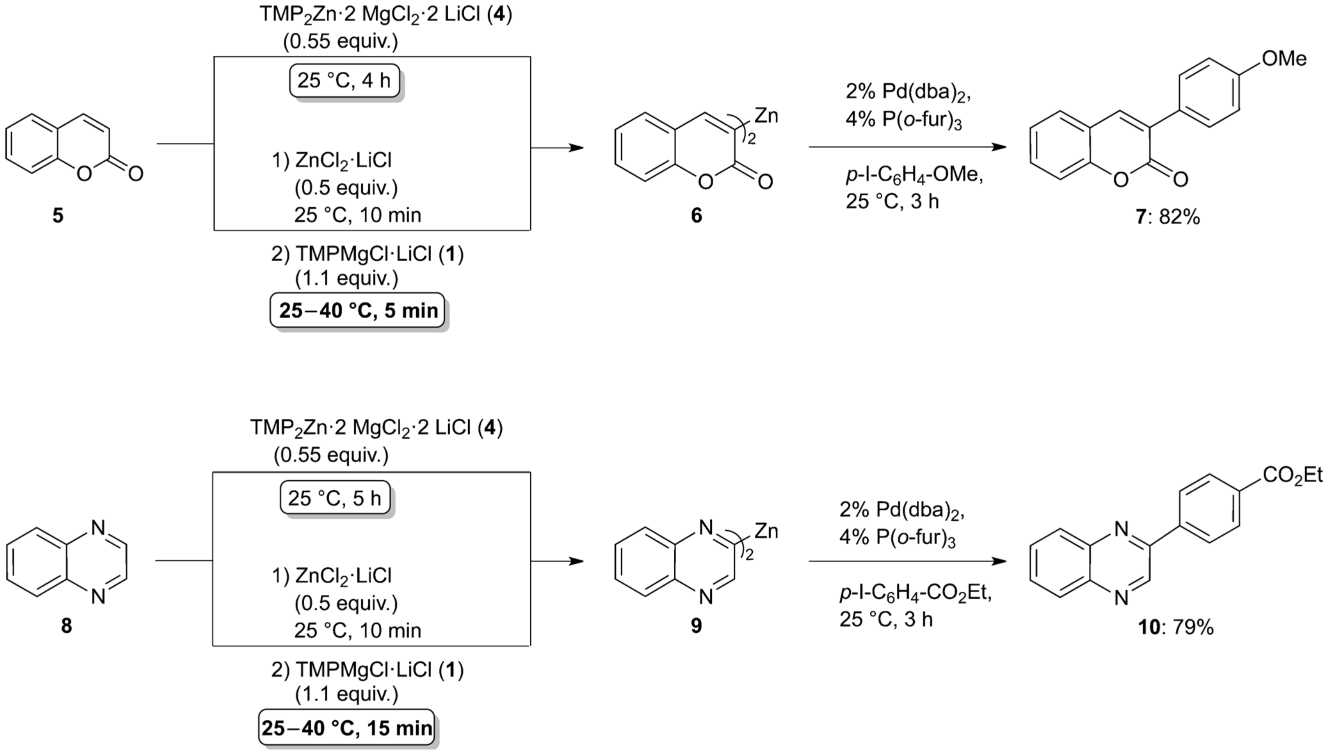


Figure 2. Progress of the metalation of quinoxaline (**8**) using different metalation procedures.

reaction can be further accelerated by addition of one extra equivalent of LiCl. Thus, if the monomeric complex $ZnCl_2 \cdot 2LiCl$[13] (0.5 equiv.) is used instead, followed by the addition of TMPMgCl·LiCl (**1**; 1.1 equiv.) **9** is obtained *within 15 min* (Figure 2).

Careful monitoring of the reaction temperature (20-mmol scale experiments) indicates that the temperature increases moderately to reach 34 °C when the addition of TMPMgCl·LiCl (**1**) to the substrate/$ZnCl_2$ solution is complete. Whereas the temperature rises to 38 °C in the case of substrate/$ZnCl_2 \cdot 2LiCl$ solution. This high rate increase in the metalation for a comparatively small temperature increase may be rationalized by an alternative reaction pathway, where the organic substrate is activated by forming



Scheme 1. Dramatic acceleration of the metalation of coumarin (**5**) and quinoxaline (**8**) with $TMP_2Zn \cdot 2MgCl_2 \cdot 2LiCl$ (**4**) and the new sequential procedure.

a Lewis acid adduct with $ZnCl_2{\cdot}2\,LiCl$ and then reacts with kinetically enhanced $TMPMgCl{\cdot}LiCl$ (**1**), to generate *in situ* an organomagnesium intermediate which can then easily transmetalate with carbophilic $ZnCl_2$ already present in the solution. On the other hand these results may be an indication for a species different from $TMP_2Zn{\cdot}2\,MgCl_2{\cdot}2\,LiCl$ (**4**) being present in the metalation. The alternative species TMP_3Zn has been proven to be unstable.[14]

Pd(0)-catalyzed cross-coupling of **9** with ethyl 4-iodobenzoate (25 °C, 3 h) furnishes the expected product **10** in 79% yield (Scheme 1).

The new procedure is quite general and by treating a variety of aromatics of type **11** and heterocycles of type **12** with $ZnCl_2{\cdot}2\,LiCl$ (0.5 equiv.), $ZnCl_2{\cdot}LiCl$ (0.5 equiv.) or $ZnCl_2$ (0.5 equiv.) followed by $TMPMgCl{\cdot}LiCl$ (**1**, 1.1 equiv., 25 °C), a range of polyfunctional diorganozincs was prepared at slightly elevated temperature, leading after a quenching with electrophiles to the expected products of type **13** in 57–94% yield (Table 1). Thus, methyl esters like methyl 4-bromo- and 4-chlorobenzoate (**11a** and **11b**) are readily zincated within 20 h providing after a copper(I)-mediated benzoylation[15] [$CuCN{\cdot}2\,LiCl$ (1.1 equiv.), PhCOCl (1.2 equiv.), −40 to 25 °C, 20 h] the corresponding keto esters **13a** and **13b** in 85–86% yield (entries 1 and 2). Interestingly, the zincation of **11a** and **11b** with $TMP_2Zn{\cdot}2\,MgCl_2{\cdot}2\,LiCl$ (**4**, 0.55 equiv.) requires a considerably longer reaction time (110 h instead of 20 h for the new procedure). Similarly, the methyl ester **11c** is zincated within 5 h and furnishes after acylation with 2-thiophenecarboxylic acid chloride the polyfunctional ketone **13c** in 82% yield (entry 3). Substituted ethyl benzoates like **11d–f** are zincated similarly. After copper(I)-mediated acylations, the ketones **13d** and **13e** are obtained in 91–94% yield (entries 4 and 5). Negishi cross-coupling of metalated **11f** with 3-iodoanisole using $Pd(dba)_2$ (2%) and $P(o\text{-fur})_3$ (4%) gave the biphenyl **13f** in 87% yield (entry 6). The zincation of 1,3-difluorobenzene (**11g**) is completed within 6 h using the new procedure (a reaction time of 90 h is required with $TMP_2Zn{\bullet}2\,MgCl_2{\bullet}2\,LiCl$ (**4**)). Copper(I)-mediated acylation with 4-chlorobenzoyl chloride furnishes the benzophenone **13g** in 80% yield (entry 7). Furthermore, various heterocycles undergo this accelerated zincation. Thus, 3,6-dimethoxypyridazine (**12a**) is metalated within 5 h. Negishi cross-coupling with ethyl 4-iodobenzoate provides the substituted pyridazine **13h** in 65% yield (entry 8). Interestingly, the heterocycles **12b** and **12c** are zincated regioselectively affording after the reactions with typical electrophiles the products **13i** and **13j** in 57–82% yield (entries 9 and 10). The metalation of the aldehyde **12d** proceeds smoothly within 2 h and iodolysis leads to the 2-iodoindole **13k** in 78% yield (entry 11). The quinoxaline **10** (see Scheme 1) can be further zincated within 2 h and a Pd(0)-catalyzed cross-coupling with 4-iodoanisole furnishes the doubly functionalized quinoxaline **13l** in 57% yield (entry 12). This method allows the zincation of *N*-Boc-protected 5-bromoindazole (**12e**) in position 3. Such a metalation is hard to achieve since usually a ring fragmentation occurs.[16] The mild conditions of the zincation procedure [(i) $ZnCl_2{\bullet}LiCl$ (0.5 equiv.), 25 °C, 10 min; (ii) $TMPMgCl{\bullet}LiCl$ (**1**, 1.1 equiv.), 25 °C, 0.1 h] lead to the 3-*z*incated indazole. Copper(I)-catalyzed acylation with 4-chlorobenzoyl chloride provides the product **13m** in 74% yield.

Remarkably, this method also allows a smooth zincation of ethyl *N*-Boc-indole-2-carboxylate (**14**) in position 3. The fast and efficient zincation procedure [(i) $ZnCl_2{\cdot}2\,LiCl$ (0.5 equiv.), 25 °C, 10 min; (ii) $TMPMgCl{\bullet}LiCl$ (**1**, 1.1 equiv.), 25 °C, 0.5 h] leads smoothly to the 3-zincated indole **15** within 30 min. Pd-catalyzed cross-coupling using 2% [1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene](3-chloropyridyl)-palladium(II) dichloride (PEPPSI-*i*-Pr)[17] as catalyst and gentle heating to 50 °C for 2 h allows the coupling with an electron-deficient aryl bromide (1.1 equiv.), providing smoothly the 3-arylated indole **16** in 81% yield. Applying our new procedure to ethyl 5-methoxybenzofuran-2-carboxylate (**17**) gives the expected zinc reagent **18** within 30 min at only moderately elevated temperature. Using the already known conditions (PEPPSI-*i*-Pr, 50 °C) the cross-coupling with 4-bromobenzonitrile is successful within 1 h providing the desired polyfunctional benzofuran **19** in 75% yield. Similarly ethyl 5-methoxybenzothiophene-2-carboxylate **20** is metalated readily under the same conditions, providing the 3-metalated benzothiophene derivative **21** after 30 min. Once more cross-coupling is achieved within 1 h at 50 °C, yielding the desired highly functionalized benzothiophene derivative **22** in 87% yield (Scheme 2).

In summary, we have reported a new zincation procedure involving the sequential addition of $ZnCl_2$ and $TMPMgCl{\cdot}LiCl$. This practical method combines fast metalations with an excellent functional group tolerance (compatibility with a methyl ester, an aldehyde and various electron-deficient heterocycles). With this method, an N^1-protected indazole scaffold can be metalated without fragmentation and undergoes readily a subsequent Cu-catalyzed acylation. This new procedure involves a metalation rate increase up to 50 times for only 10–15 °C temperature increase, indicating either a reaction pathway including a Lewis acid activation of the organic substrate, followed by a magnesiation and a fast transmetalation with $ZnCl_2$ or that a more reactive species could be generated at this moderately elevated temperature. Further studies along these lines are underway in our laboratories.

Table 1. Products obtained by using the stepwise metalation procedure with $ZnCl_2 \cdot n LiCl$ ($n = 0, 1, 2$) and TMPMgCl·LiCl (**1**).[a]

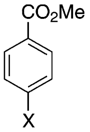
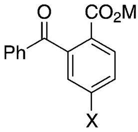
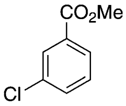
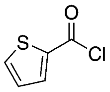
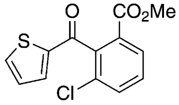
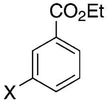
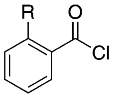
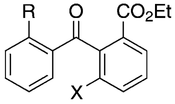
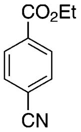
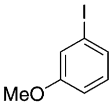
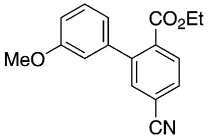
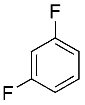
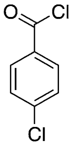
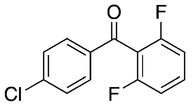
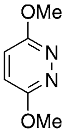
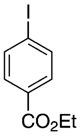
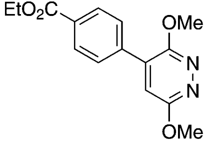
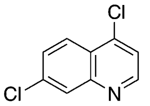
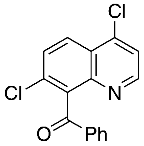
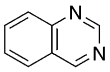
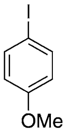
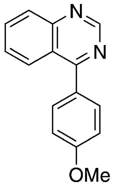
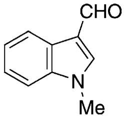
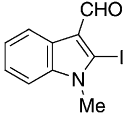
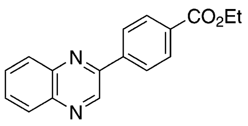
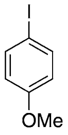
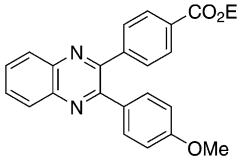
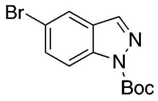
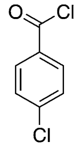
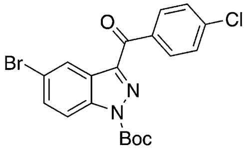
	Substrate; Time [h][b]	E^+	Product; Yield[c]
1	 **11a**: X = Br, $n = 0$; 20 (110)	PhCOCl	 **13a**: X = Br; 85%[d]
2	**11b**: X = Cl, $n = 0$; 20 (110)		**13b**: X = Cl; 86%[d]
3	 **11c**: $n = 0$; 5 (36)		 **13c**; 82%[d]
4	 **11d**: X = Br, $n = 0$; 4 (72)		 **13d**: X = Br; R = H; 91%[d]
5	**11e**: X = F, $n = 0$; 2 (12)		**13e**: X = F; R = Cl; 94%[d]
6	 **11f**: $n = 0$; 3 (25)		 **13f**; 87%[e]
7	 **11g**: $n = 0$; 6 (90)		 **13g**; 80%[d]
8	 **12a**: $n = 0$; 5		 **13h**; 65%[e]
9	 **12b**: $n = 1$; 0.1	PhCOCl	 **13i**; 82%[d]
10	 **12c**: $n = 1$; 1		 **13j**; 57%[e]
11	 **12d**: $n = 1$; 2	I_2	 **13k**; 78%

Table 1. (Continued)

	Substrate; Time [h][b]	E+	Product; Yield[c]
12	 **10**: $n=2$; 2		 **13l**; 57%[e]
13	 **12e**: $n=2$; 0.1		 **13m**; 74%[d]

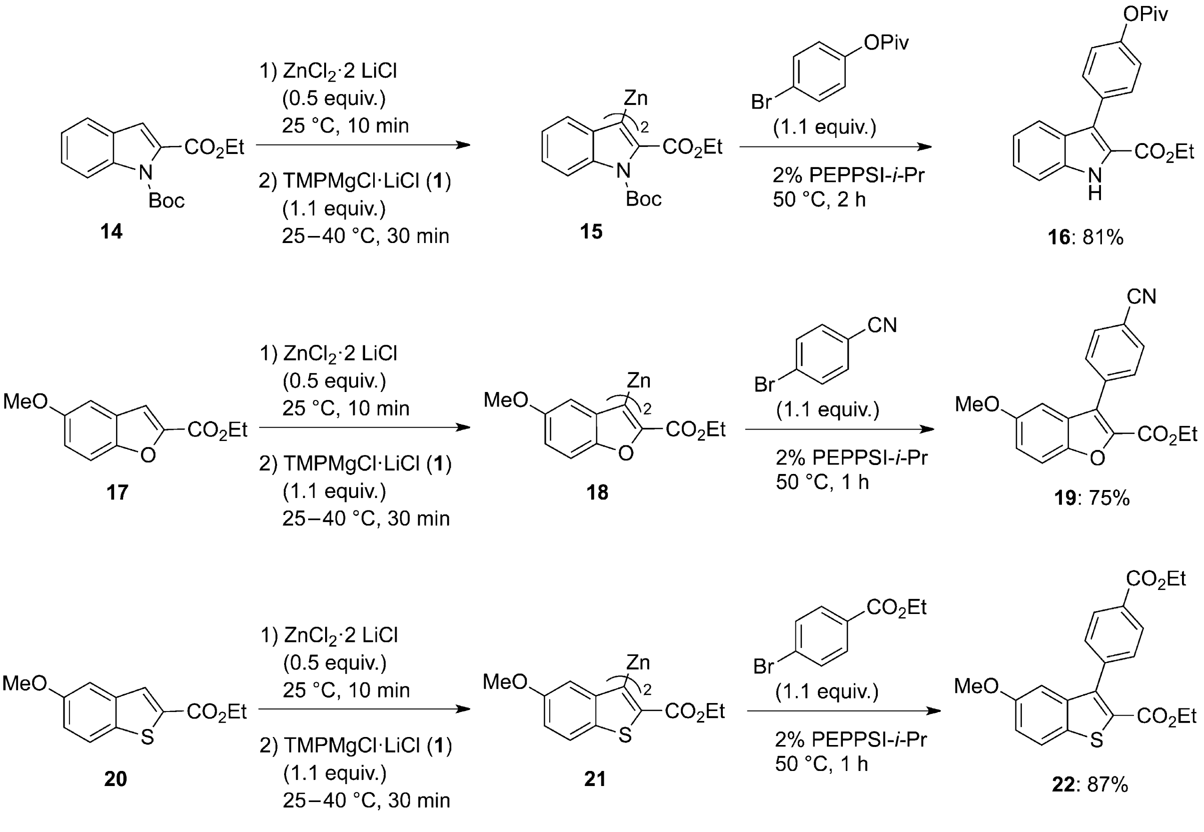
[a] *Reactions conditions*: 2 mmol substrate, 2 mL THF, 1 mL 1 M $ZnCl_2 \cdot nLiCl$ solution, 2 mL 1.2 M TMPMgCl·LiCl solution.

[b] In parentheses are given the metalation times using $TMP_2Zn \cdot 2MgCl_2 \cdot 2LiCl$ (**4**) (0.55 equiv.).

[c] Isolated yield of analytically pure product.

[d] A transmetalation with CuCN•2LiCl (1.1 equiv.) was performed.

[e] Obtained by palladium-catalyzed cross-coupling using $Pd(dba)_2$ (2%) and $P(o\text{-fur})_3$ (4%).



Scheme 2. Expeditive zincation at position 3 of indole, benzofuran and benzothiophene derivatives.

Experimental Section

Synthesis of 2-Benzoyl-4-bromobenzoic Acid Methyl Ester (13a)

A dry and argon-flushed 25-mL Schlenk tube, equipped with a magnetic stirring bar was charged with a solution of methyl 4-bromobenzoate (**11a**; 428 mg, 2.0 mmol) in dry THF (1 mL) and treated with $ZnCl_2$ (1 M solution in THF, 1.0 mL, 1.0 mmol). TMPMgCl·LiCl (1.2 M in THF, 1.85 mL, 2.2 mmol) was added dropwise and the reaction mixture was stirred at 25 °C for 20 h. The reaction mixture was cooled to −40 °C, then CuCN·2LiCl (1 M in THF, 2.2 mL, 2.2 mmol) and benzoyl chloride (0.28 mL, 2.4 mmol) were added. The mixture was allowed to warm to 25 °C and stirred overnight. The reaction mixture was quenched with a saturated aqueous NH_4Cl solution (10 mL), extracted with diethyl ether (3×20 mL) and dried over $MgSO_4$. After filtration, the solvent was evaporated under vacuum. The crude product was purified by column chromatography (pentane:ether = 6:1) to give **13a** as a yellow solid; yield: 542 mg (85%).

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