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Preparation of Polyfunctional Naphthyridines by Cobalt-Catalyzed Cross-Couplings of Halogenated Naphthyridines with Magnesium and Zinc Organometallics

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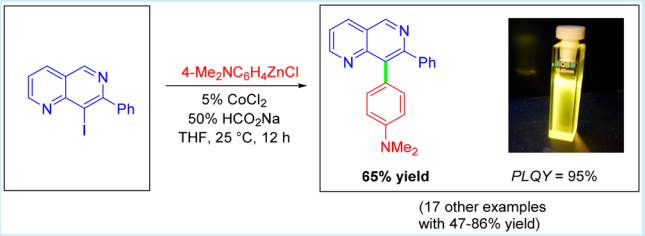
Supporting Information

ABSTRACT: $CoCl_2$ (5%) catalyzes cross-couplings of various halogenated naphthyridines with alkyl- and arylmagnesium halides. Also, arylzinc halides undergo smooth cross-couplings with various naphthyridines in the presence of $CoCl_2$·2LiCl (5%) and sodium formate (50%), leading to polyfunctional arylated naphthyridines. Two of these arylated naphthyridines are highly fluorescent, with quantum efficiencies reaching 95% and long excited-state lifetimes of up to 12 ns.



N-Heterocyclic scaffolds are ubiquitous building blocks for pharmaceuticals, agrochemicals, and materials science.[1] There is a need for new N-heterocyclic structures since novel ring systems may display original biological or physical properties. Recently, the naphthyridine scaffold has attracted increased attention.[2] Its functionalization was found to be especially difficult, and only a few methods are available.[3] Although Fe-catalyzed cross-couplings have been used to functionalize chloronaphthyridines, the scope of such cross-couplings is quite limited.[4] Interestingly, Co-catalyzed cross-couplings generally display a broader reaction scope and have proved to be very useful for the functionalization of electron-deficient N-heterocycles.[5] We recently showed that the addition of appropriate ligands (e.g., sodium formate or pivalate) considerably extends the scope of these cross-couplings.[6] Herein we report that Co-catalyzed cross-couplings allow efficient functionalization of various halogenated naphthyridines.

In preliminary experiments, we found that chloronaphthyridines **1a**–**c** are easily alkylated using 5% $CoCl_2$ in THF (Table 1). Thus, the reaction of 3,6-dichloro-1,8-dimethyl-2,7-naphthyridine (**1a**) with 2-phenylethylmagnesium bromide (**2a**) at 25 °C (30 min) provided monoalkylated naphthyridine **3a** in 80% yield (Table 1, entry 1). Similarly, alkylmagnesium reagent **2a** allowed the conversion of 1-chloro-2,7-naphthyridine (**1b**) to the expected 1-phenethyl-2,7-naphthyridine (**3b**) in 82% yield (entry 2). Treatment of **1b** with MeMgCl (**2b**) gave the corresponding 1-methyl-2,7-naphthyridine (**3c**) in 98% yield (entry 3). Furthermore, *sec*-BuMgCl (**2c**) underwent cross-coupling with **1b** to afford 2,7-naphthyridine **3d** in 54% yield (entry 4). Co-catalyzed alkylation of 5-chloro-1,6-naphthyridine **1c** with BuMgCl (**2d**) provided 1,6-naphthyridine **3e** in 69% yield (entry 5). Additionally, the reaction of 5-chloro-1,6-naphthyridine **1c** with cyclopropylmagnesium bromide (**2e**) gave 1,6-naphthyridine **3f** in 52% yield (entry 6).

Furthermore, we have found that 3,6-dichloronaphthyridine **1a** was easily bisarylated in the presence of 5% $CoCl_2$ using arylmagnesium reagents[7] such as **4a**–**d** (Scheme 1). Thus, the reaction of **1a** with 4-trimethylsilylphenylmagnesium bromide (**4a**) (3.0 equiv) at −40 °C provided bisarylated 2,7-naphthyridine **5a** in 62% yield within 4 h. Similarly, 4-*N*,*N*-dimethylaminophenylmagnesium bromide (**4b**) and 4-anisylmagnesium bromide (**4c**) underwent Co-catalyzed cross-couplings (−40 °C, 4–12 h) with **1a**, leading to 3,6-substituted naphthyridines **5b** and **5c**, respectively, in 60–73% yield. Sterically hindered mesitylmagnesium bromide (**4d**), however, reacted with **1a** at 25 °C within 4 h, furnishing 2,7-naphthyridine **5d** in 93% yield.

We noticed that $C(sp^2)$–$C(sp^2)$ cross-couplings of naphthyridines **1b** and **1c** with PhMgCl using 5% $CoCl_2$ led to low yields (<30%). This problem could be solved by replacing arylmagnesium halides with the corresponding arylzinc reagents and using HCO_2Na as a ligand.[6a] Thus, **1b** reacted smoothly with PhZnCl (**6a**) or [1,1′-biphenyl]-4-ylzinc chloride (**6b**) within 12 h at 25 °C, furnishing the corresponding arylated naphthyridines **7a** and **7b** in 80–82% yield (Table 2, entries 1 and 2). Furthermore, a range of arylzinc reagents **6c**–**f** bearing various functional groups underwent such Co-catalyzed Negishi[8] cross-couplings with **1b**, providing the expected products **7c**–**f** in 69–79% yield (entries 3–6). Heteroaryl–heteroaryl cross-couplings are utmost challenging because of catalyst deactivation when Pd or Ni catalysts are used.[9] However, in the presence of THF-soluble $CoCl_2$·2LiCl (5%) and HCO_2Na (50%), the cross-

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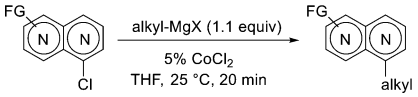
Table 1. Co-Catalyzed Alkylation of Chloronaphthyridines 1a–c with Alkylmagnesium Reagents 2a–e

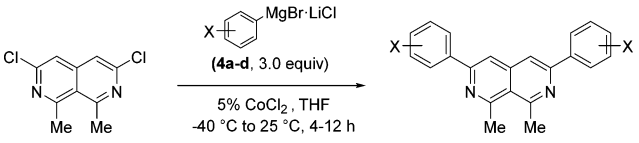


1a-c FG = H, Cl, CF_3, Me; X = Cl, Br **3a-f**

entry	naphthyridine	RMgX	product[a], yield (%)
1	**1a**	**2a**; R = $Ph(CH_2)_2$	**3a**, 80
2	**1b**	**2a**; R = $Ph(CH_2)_2$	**3b**, 82
3	**1b**	**2b**; R = Me	**3c**, 98
4	**1b**	**2c**; R = *s*-Bu	**3d**, 54
5	**1c**	**2d**; R = Bu	**3e**, 69
6	**1c**	**2e**; R = *c*-Pr	**3f**, 52

[a]Isolated yields of analytically pure products.

Scheme 1. Co-Catalyzed Bisarylation of Naphthyridine 1a with Various Arylmagnesium Bromides (4a–d)

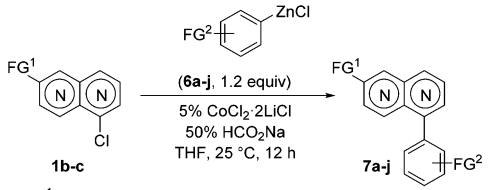


1a

5a: X = 4-$SiMe_3$; 62%
5b: X = 4-NMe_2; 73%
5c: X = 4-OMe; 60%
5d: X = 2,4,6-Me; 93%

coupling of 1-chloronaphthyridine **1b** with 2-thienylzinc chloride (**6g**) afforded 2,7-naphthyridine **7g** in 60% yield (entry 7). We further have shown that naphthyridine **1c** was easily arylated under these conditions. Thus, the reaction of **1c** with arylzinc chlorides **6h** and **6i** provided 1,6-naphthyridines **7h** and **7i**, respectively, in 74–83% yield (entries 8 and 9). Interestingly, the Co-catalyzed arylation of **1c** with 2-(triisopropylsilyloxy)-phenylzinc chloride (**6j**) succeeded at only elevated temperature (60 °C, 12 h) to give naphthyridyl alcohol derivative **7j** in 61% yield (entry 10). Also, iodo-substituted naphthyridines were excellent substrates for such Co-catalyzed cross-couplings. Thus, the reaction of electron-rich arylzinc reagents **6k** and **6l** with 4-iodo-1,5-naphthyridine (**1d**) afforded 1,5-naphthyridines **7k** and **7l**, respectively, in 78–80% yield (Table 3, entries 1 and 2). Similarly, the reaction of electron-deficient *p*-NCC_6H_4ZnCl (**6m**) with **1d** led to naphthyridine **7m** in 83% yield (entry 3). Furthermore, heteroarylzinc reagent **6n** reacted smoothly with **1d** to afford naphthyridine **7n** in 73% yield (entry 4). Remarkably, sterically demanding naphthylzinc reagent **6o** was also converted with **1d** to 1,5-naphthyridine **7o** in 47% yield (entry 5).

Table 2. Co-Catalyzed Arylations of Arylzinc Reagents 6a–j with Chloronaphthyridines 1b and 1c



1b-c **7a-j**

FG^1 = H, CF_3
FG^2 = H, OMe, OTBS, OTIPS, OBn, CN, F, CF_3, SMe, Ph, Me

entry	naphthyridine	zinc reagent	product[a], yield (%)
1	**1b**	**6a**; X = H	**7a**, 80
2	**1b**	**6b**; X = *p*-Ph	**7b**, 82
3	**1b**	**6c**; X = *p*-CF_3	**7c**, 69
4	**1b**	**6d**; X = *p*-OTBS	**7d**, 72
5	**1b**	**6e**; X = *p*-CN, *m*-F	**7e**, 74
6	**1b**	**6f**	**7f**, 79
7	**1b**	**6g**	**7g**, 60
8	**1c**	**6h**	**7h**, 74
9	**1c**	**6i**; X = *p*-OBn	**7i**, 83
10	**1c**	**6j**; X = *o*-OTIPS	**7j**, 61[b]

[a]Isolated yields of analytically pure products. [b]The cross-coupling reaction proceeded at 60 °C for 12 h.

This mild method also allows the coupling of sensitive iodonaphthyridines. Thus, the coupling of zinc reagent **6p** with 4-iodo-1,5-naphthyridine **1e** provided the corresponding 4,8-functionalized 1,5-naphthyridine **7p** in 86% yield (entry 6). Similarly to the bisarylation of dichloronaphthyridine **1a** (Scheme 1), we also examined the Co-catalyzed reaction of 2,4-diiodo-1,5-naphthyridine (**1f**) with *p*-$MeOC_6H_4ZnCl$ (**6l**) and obtained the corresponding bis(anisyl)naphthyridine **7q** in 75% yield (entry 7). Finally, Co-catalyzed cross-coupling of

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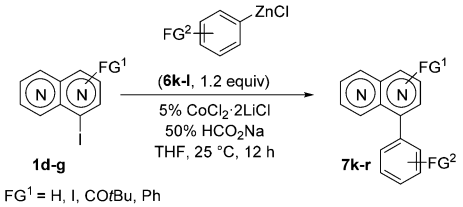
Table 3. Co-Catalyzed Arylations of Arylzinc Reagents 6k and 6l with Iodonaphthyridines 1d−g

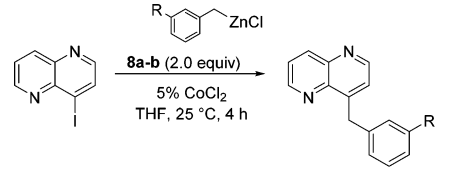


entry	naphthyridine	zinc reagent	product[a], yield (%)
1	**1d**	**6k**; X = *m*-SMe	**7k**, 80
2	**1d**	**6l**; X = *p*-OMe	**7l**, 78
3	**1d**	**6m**; X = *p*-CN	**7m**, 83
4	**1d**	**6n**	**7n**, 73
5	**1d**	**6o**	**7o**, 47
6	**1e**	**6p**	**7p**, 86
7	**1f**	**6l**	**7q**[b], 75
8	**1g**	**6p**	**7r**[c], 65

[a]Isolated yields of analytically pure products. [b]2.4 equiv of zinc reagent was used. *p*-An = *p*-MeOC$_6$H$_4$. [c]3.0 equiv of the arylzinc reagent was necessary for complete conversion.

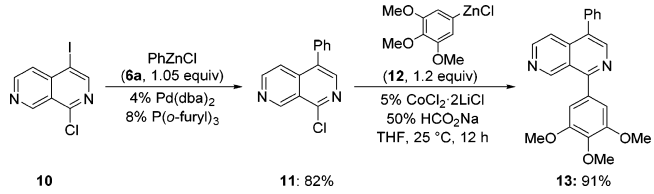
sterically hindered 8-iodo-1,6-naphthyridine (**1g**)[10] with *p*-Me$_2$NC$_6$H$_4$ZnCl (**6p**) furnished naphthyridine **7r** in 65% yield (entry 8). We also found that **1d** smoothly reacts with benzylic zinc reagents.[11] Thus, the couplings of **1d** with benzylzinc chlorides **8a** and **8b** provided 1,5-naphthyridines **9a** and **9b** in 62−75% yield (Scheme 2).

Scheme 2. Co-Catalyzed Cross-Coupling of 4-Iodo-1,5-naphthyridine (1d) with Benzylic Zinc Reagents 8a and 8b



By using mixed halogenated naphthyridines, we observed that 1-chloro-4-iodo-2,7-naphthyridine (**10**) was regioselectively functionalized by stepwise cross-coupling utilizing successive Pd and Co catalyses (Scheme 3). Thus, Pd-catalyzed Negishi

Scheme 3. Regioselective Pd/Co-Catalyzed Cross-Coupling



cross-coupling of **10** with PhZnCl (**6a**) selectively furnished 2,7-naphthyridine **11** in 82% yield. Subsequent Co-catalyzed cross-coupling with arylzinc chloride **12** gave the mixed bisarylated naphthyridine **13** in 91% yield.

Naphthyridine derivatives have previously been applied as fluorescent probes[12] or as ligands for fluorescent complexes.[13] The newly prepared naphthyridines **5b** and **7r** are highly fluorescent in various organic solvents and display strong solvatochromism (Figure 1a,b and Supporting Information (SI) Figures 1−4). We suggest that these phenomena are based on strong interactions between the electron donor NMe$_2$ and the electron-poor naphthyridine moiety as an electron acceptor. While the absolute photoluminescence quantum efficiencies (PLQEs) of **5b** in various solvents are about 20%, the PLQE of **7r** is almost quantitative in nonpolar solvents (toluene, 95 ± 5%; cyclohexane, 93 ± 5%) and drops only slightly in more polar solvents ($CHCl_3$, 81 ± 5%; 1,4-dioxane, 80 ± 5%; THF, 71 ± 5%; see SI Figures 5 and 6 for details). These high emission efficiencies are accompanied by very long excited lifetimes of 3.8 and 12.0 ns for **5b** and **7r**, respectively (Figure 1c,d; see the SI for details).

In summary, we have prepared various novel polyfunctionalized naphthyridines by Co-catalyzed cross-couplings. Alkyl- and arylmagnesium reagents reacted smoothly with chloro-2,7-naphthyridines using $CoCl_2$ (5%). The addition of sodium formate allowed an extension of the range of functionalized N-heterocycles by mild cross-coupling of chloro- and iodonaphthyridines with arylzinc reagents. Two of the new naphthyridines are highly fluorescent (PLQE = 20−95%) with tunable emission from blue to yellow and long excited-state lifetimes from 3.8 to 12.0 ns. Further extensions of organometallic naphthyridine functionalizations are currently underway in our laboratories.

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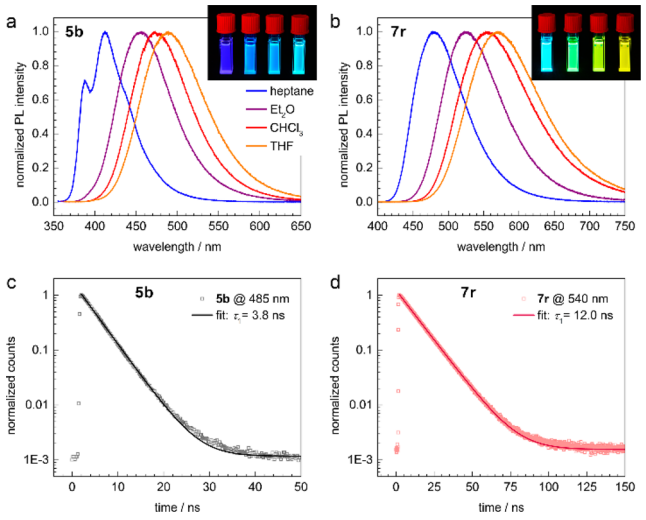

Figure 1. (a, b) PL spectra of compounds **5b** and **7r**, respectively, dissolved in heptane (blue), Et_2O (purple), $CHCl_3$ (red), and THF (orange). The excitation wavelengths were 360 and 390 nm, respectively. The insets show photographs of the solutions under UV illumination. (c, d) Time-correlated single-photon counting (TCSPC) traces of **5b** and **7r** in $CHCl_3$, measured at the peaks of the PL spectra (open symbols). The solid lines are monoexponential fits.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b03242.

Experimental details, GC data, melting points, and IR, ^1H and ^{13}C NMR, and mass spectra (PDF)

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Notes

The authors declare no competing financial interest.

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