# <u>Creanic</u> LETTERS

# Cu-Catalyzed Aerobic Oxidative C–H/C–O Cyclization of 2,2'-Binaphthols: Practical Synthesis of PXX Derivatives

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# **Supporting Information**

**ABSTRACT:** Cu-catalyzed C-H/C-O cyclization of 2,2'-binaphthol, using air as an oxidant, was developed. C-H functionalization of binaphthols occurred at the 8,8'-position to form *peri*-xanthenoxanthenes that exhibit high charge-carrier mobility. The reaction can tolerate a wide variety of functional groups and afforded the corresponding *peri*-xanthenoxanthene derivatives via an efficient procedure.



*peri*-Xanthenoxanthene (PXX) is an O-containing sixmembered aromatic compound that exhibits high carrier mobility and good environmental stability;<sup>8–13</sup> therefore, PXXbased molecules have been studied as electronically attractive materials. 3,7-Bis(*p*-propylphenyl)PXX has been employed as a *p*-type thin-film transistor in a rollable display by Kobayashi (Sony Corporation).<sup>8</sup> Furthermore, PXX-containing conducting polymers were reported by Swager<sup>10a</sup> and Li,<sup>10b</sup> and PXX-based polycyclic aromatic hydrocarbons were synthesized by Bonifazi.<sup>11</sup>

Despite the utility of PXX derivatives, the synthetic methodology of PXX compounds has been less developed. The preparation of PXX has been restricted to oxidative cyclization of 1,1'-bi-2-naphthol (1a) with a (sub)stoichiometric oxidant  $[Cu(OAc)_{2}^{9a} CuO_{2}^{9e} MnO_{2}^{9e} CuI/PivOH_{1}^{11} Hg(NMe_{3})_{2}^{12}$ and NOBF<sub>4</sub><sup>10a</sup>] or nucleophilic aromatic substitution of perfluoro-1,1'-bi-2-naphthol (Scheme 1).<sup>13</sup> The lack of a practical, catalytic, and efficient synthetic methodology for the synthesis of PXX slowed down the research on PXX-based materials.

#### Scheme 1. Syntheses of PXX Derivatives





In this decade, metal-catalyzed intramolecular C–H/C–O cyclization for the construction of oxygen-containing heterocycles has been widely reported. Although various metal catalysts were utilized for this transformation,<sup>14</sup> Cu-catalyzed cyclization has been well-developed for C–O bond formation.<sup>15–23</sup> In 2008, a landmark study on intramolecular C–H/C–O cyclization was established by Nakazawa to synthesize benzoxazoles from benzanilides.<sup>16</sup> Other examples of Cu-catalyzed intramolecular C–O bond-forming reactions were used to prepare oxazoles,<sup>17</sup> dibenzofurans,<sup>18</sup> tetrahydrofurans,<sup>19</sup> 4*H*-3,1-benzoxadines,<sup>20</sup> dihydrooxazinones,<sup>21</sup> benzolactones,<sup>22</sup> and cyclic purine nucleosides.<sup>23</sup>

Herein, we report a practical catalytic cyclization of 1,1'-bi-2naphthols that leads to PXX derivatives. The stoichiometric reaction has already been reported, and the key step of this transformation was determined as the reoxidation of the Cu catalyst. Although many oxidants such as  $K_2S_2O_8$ ,  $(NH_4)_2S_2O_8$ ,  $(BzO)_2$ , and Ag salts have been used for the reoxidation of Cu catalysts, molecular oxygen is considered as the most environmentally friendly option. Thus, molecular oxygen in air should be adopted as the general and conventional oxidant for the synthesis of PXX derivatives.

The initial reaction was carried out in the presence of 30 mol % of CuCl and 2 equiv of  $K_2CO_3$  in *m*-xylene at 120 °C for 20 h under air to afford the desired PXX (**2a**) in 34% yield; unchanged **1a** was also recovered (Scheme 2).

The results indicate that the reoxidation step did not work well without the ligands of a Cu catalyst. Electron-donating ligands such as N-based and N-heterocyclic carbene (NHC) ligands are









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known as effective ligands to accelerate aerobic oxidation of the metal catalyst.<sup>24,25</sup> As shown in Table 1, we investigated the



# ligands in this reaction. Bidentate N-based ligands, such as 2,2'bipyridine (entry 2) and 1,10-phenanthroline (entry 3), afforded 2a in lower yields. The lower reactivity of the bidentate ligands was attributed to the occupation of the coordination sites of the Cu catalyst that decreases the reactivity of binaphthol cyclization. Thus, electron-donating monodentate ligands were also evaluated. The NHC ligand IPr was also ineffective (entry 4), whereas pyridine slightly increased the yield of the product (entry 5). N-Methylimidazole (NMI), reported by Stahl as the best ligand for Cu-catalyzed aerobic oxidation of alcohols,<sup>25</sup> accelerated the reaction effectively to afford 2a in 92% yield (entry 6). When the reaction was performed under $N_2$ , the yield of 2a was diminished to 37% (entry 7).<sup>26</sup> These results suggest that molecular oxygen in air oxidizes the Cu catalyst successfully with the aid of the NMI ligand. These conditions only accelerate the reoxidation step of the Cu catalyst and not the cyclization of 1a.

Cu precursors (Table 2) were screened next. The use of CuBr (entry 2) and CuI (entry 3) as Cu(I) catalysts did not improve

#### Table 2. Screening of Cu Catalysts

Ta starting of the starting of	DH 30 mol % Cu cat. 60 mol % NMI DH 2 equiv K <sub>2</sub> CO <sub>3</sub> <i>m</i> -xylene, air 120 °C, 20 h	2a
entry	Cu catalyst	yield (%)
1	CuCl	92
2	CuBr	41
3	CuI	50
4	CuO	36
5	$CuCl_2$	72
6	$Cu(OAc)_2$	35
7	$Cu(OTf)_2$	62
8 <sup>a</sup>	CuCl	71
9		0 <sup>b</sup>
10	CuCl <sup>c</sup>	87
$11^{d,e}$	CuCl	71

<sup>a</sup>At 100 °C. <sup>b</sup>Recovered 1a. <sup>c</sup>Without K<sub>2</sub>CO<sub>3</sub>. <sup>d</sup>At 4 g (15 mmol) scale. <sup>c</sup>For 30 h.

the yield of **2a**. Moreover, Cu(II) precursors, such as CuO (entry 4), CuCl<sub>2</sub> (entry 5), Cu(OAc)<sub>2</sub> (entry 6), and Cu(OTf)<sub>2</sub> (entry 7), reduced the efficiency of the cyclization. The reaction performed at 100 °C exhibited lower reactivity to afford **2a** in 71% yield (Table 2, entry 8). When CuCl was omitted, the reaction did not proceed and **1a** was recovered (entry 9). The reaction without K<sub>2</sub>CO<sub>3</sub> also gave the product, albeit in slightly lower yield (entry 10). Large-scale synthesis (4 g, 15 mmol) needed longer reaction time to afford the product in good yield (entry 11).

We next focused on the extension of the scope of functionalized binaphthols. The reaction was performed with 40 mol % of CuCl and 80 mol % of NMI due to reduced efficiency of the Cu catalyst (Table 3). Silyl groups at the 3,3'-position of binaphthol were tolerated under these conditions,

#### Table 3. Scope and Limitation



"At 140 °C. "Without K2CO3. "With 20 mol % of CuCl and 40 mol % of NMI.

affording 5,11-bis(trimethylsilyl)PXX (**2b**) in high yield (entry 1). Cyclization with other substrates bearing alkyl (entry 2), allyl (entry 3), phenyl (entry 4), and ester (entry 5) groups at the 3,3'-position also proceeded to afford the corresponding product in good yield. Tetraalkylbinaphthol was subjected to these conditions to yield the corresponding product (entry 6). The reaction with a binaphthol comprising an alkyl (entry 7) group at the 7,7'-position also afforded the corresponding PXX derivative. 6,6'-Diarylbinaphthol subjected to these reaction conditions afforded the product in good yield (entry 8).

We established that the CuCl/NMI system was the best catalyst for aerobic C–H/C–O cyclization of binaphthol derivatives. This catalyst system is well-known in other Cucatalyzed oxidative transformation reactions.<sup>27–29</sup> Notably, Yu and Xie reported the homocoupling reaction of 3-ethoxycarbonyl-2-naphthol using a CuCl<sub>2</sub>/NMI system.<sup>28a</sup> Taking this report into consideration, we realized a one-pot construction of PXX from 2-naphthol (Scheme 3). The reaction successfully proceeded in *m*-xylene at 140 °C to afford **2a** from **1a** in high yield.

Scheme 3. One-Pot Oxidative Coupling/Cyclization for the Synthesis of PXX from 2-Naphthol



We proposed a reaction mechanism via single electron transfer (Scheme 4) based on the Cu-mediated C-H functionalization





established by Yu.<sup>30</sup> When the reaction with monomethyl binaphthol 3 was performed, the corresponding product was not detected (Scheme 5). In this mechanism, the hydroxy groups act as directing and electron-donating groups. K<sub>2</sub>CO<sub>3</sub> accelerates the deprotonation of binaphthol and ligand exchange of the Cu catalyst. Nucleophilic substitution mechanism (S<sub>N</sub>Ar)<sup>13</sup> could not be ruled out because under an inert atmosphere and a Cu(I)

Scheme 5. Reaction with Methyl-Protected Binaphthol



catalyst, the reaction still afforded the product, albeit in lower yields.

Photochemical and electrochemical properties of newly synthesized PXX derivatives are shown in Table 4. UV-vis

Table 4. Photochemical and Electrochemical Properties ofPXX Derivatives

2	$\lambda_{abs}^{a}$ (nm)	$\lambda_{\rm em}^{a,c}$ (nm)	$\Phi_{\mathfrak{fl}}^{}c,d}$ (%)	$E_{ox}^{e}$ (V)	$E_{\rm HOMO}^{f}$ (eV)	$E_{LUMO}^{g}$ (eV)
2a	442 <sup>b</sup>	450		0.810	-5.21	-2.43
2c	439	450	33.1	0.767	-5.16	-2.38
2d	441	450	22.6	0.777	-5.17	-2.39
2e	453	465	22.1	0.980	-5.38	-2.68
2f	480	505	12.8	0.833	-5.23	-2.39
2g	442	454	11.9	0.596	-5.00	-2.23
2h	446	454	29.0	0.686	-5.08	-2.32
2i	447	453	26.3	0.816	-5.21	-2.45

<sup>*a*</sup>Measured in CH<sub>2</sub>Cl<sub>2</sub> solution (1 × 10<sup>-5</sup> M). <sup>*b*</sup>Measured in CH<sub>2</sub>Cl<sub>2</sub> solution (1 × 10<sup>-4</sup> M). <sup>*c*</sup>Excited at  $\lambda_{abs}$ . <sup>*d*</sup>Quantum yield measured in CH<sub>2</sub>Cl<sub>2</sub> solution (1 × 10<sup>-3</sup> M). <sup>*e*</sup>Half-wave potentials, determined by CV in 0.1 M solution of Bu<sub>4</sub>NPF<sub>6</sub> in CH<sub>2</sub>Cl<sub>2</sub>; vs Ag/Ag<sup>+</sup>. <sup>*f*</sup>Estimated vs vacuum level from  $E_{HOMO} = -4.4 \text{ eV} - E_{ox}$ . <sup>*g*</sup>E<sub>LUMO</sub> =  $E_{HOMO} + E_{g'}$  where  $E_{g}$  = optical gap, calculated from the optical absorption/ emission data.

absorption and mirror-plane symmetrical emission spectra (Figures S1–S8) indicate the rigid, planar  $\pi$ -system of these PXX derivatives. Spectra of **2f** are red-shifted compared with other PXX derivatives, which shows the delocalization of electrons on the aromatic ring with an electron-withdrawing ester group. All PXX derivatives exhibited reversible one-electron oxidation peak, which indicates the good electrical stability of PXX radical cation (Figures S9–S16a). However, **2a** and **2h** showed an irreversible two-electron oxidation CV curve within the range of 0 to 2.0 V (Figures S9b and S15b).

In summary, we have developed the first catalytic synthesis of PXX derivatives using a CuCl/NMI system. This protocol provides practical and simple access to electronically important PXX compounds from binaphthol derivatives whose synthetic methods have been widely studied in the field of asymmetric synthesis. The one-pot synthesis of PXX from binaphthol using the same catalyst was also proposed. The reaction could be performed under air, and the NMI ligand accelerated the reoxidation step of the Cu catalyst.

### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b01060.

Experimental procedures and NMR data (PDF)

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The authors declare no competing financial interest.

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